

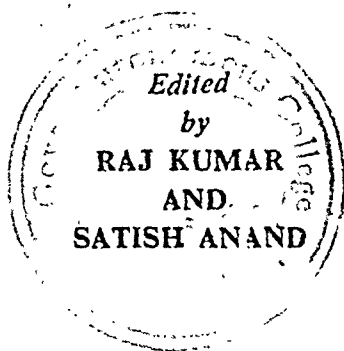
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DICTIONARY  
OF  
ANALYTICAL CHEMISTRY

# DICTIONARY OF ANALYTICAL CHEMISTRY



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# Preface

This dictionary includes the most frequently used terms which have been carefully selected from the various fields of analytical chemistry such as spectroscopy, volumetric Analysis, Gravimetric Analysis, Electroanalytical Analysis, Qualitative Analysis etc.

Every attempt has been carefully made to write the entries in a clear and lucid style to provide both straight forward definitions and invaluable background information. At some appropriate places, line diagrams have been included whenever the meaning of a word can be best understood by means of a diagram.

This dictionary will be of immense value to undergraduate and post-graduate chemistry students. It will be also of value to the students of analytical chemistry, biochemistry, medicine, pharmacy and others studying or working in related fields.

When a dictionary of this kind is being compiled, it becomes essential to draw upon the work of many authorities and seek the advice of colleagues to all of whom the editors are deeply indebted.

Finally, the editors express their sincere thanks to the publishers and printer for printing this book promptly.

All comments from users on omissions or shortcomings will be most welcome.

EDITORS

# A

**Abel Tester.** A laboratory instrument used in testing the flash point of kerosine and other volatile oils having flash points below 120°F (49°C); the oil is contained in a closed cup which is heated by a fixed flame below and a movable flame above.

**Absolute Gravity.** Density or specific gravity of a fluid reduced to standard conditions; for example, with gases, to 760 mmHg pressure and 0°C temperature. Also known as absolute density.

**Absorbance.** The common logarithm of the reciprocal of the transmittance of a pure solvent. Also known as absorbancy; extinction.

**Absorbancy.** See absorbance.

**Absorbency Index.** See absorptivity.

**Absorber.** Equipment in which a gas is absorbed by contact with a liquid.

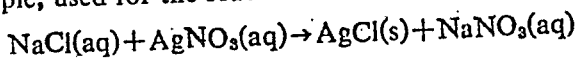
**Absorptiometer**

1. An instrument equipped with a filter system or other simple dispersing system to measure the absorption of nearly monochromatic radiation in the visible range by a gas or a liquid, and so determine the concentration of the absorbing constituents in the gas or liquid.
2. A device for regulating the thickness of a liquid in spectrophotometry.

**Absorptiometric Analysis.** Chemical analysis of a gas or a liquid by measurement of the peak electromagnetic absorption wavelengths that are unique to a specific material or element.

**Absorption Edge.** The wavelength corresponding to a discontinuity in the variation of the absorption coefficient of a substance with the wavelength of the radiation. Also known as absorption limit.

**Absorption Indicator.** A type of indicator used in reactions that involve precipitation. The yellow dye fluorescein is a common example, used for the reaction



As silver nitrate solution is added to the sodium chloride, silver chloride precipitates. As long as  $\text{Cl}^-$  ions are in excess, they adsorb on the precipitate particles. At the end point, no  $\text{Cl}^-$  ions are left in solution and negative fluorescein ions are then adsorbed, giving a pink colour to the precipitate.

**Absorption Limit.** See absorption edge.

**Absorption Line.** A minute range of wavelength or frequency in the electromagnetic spectrum within which radiant energy is absorbed by the medium through which it is passing.

**Absorption Peak.** A wavelength of maximum electromagnetic absorption by a chemical sample; used to identify specific elements, radicals, or compounds.

**Absorption Plant.** A facility to recover the condensable portion of natural or refinery gas.

**Absorption Spectrophotometer.** An instrument used to measure the relative intensity of absorption spectral lines and bands. Also known as difference spectrophotometer.

**Absorption Spectroscopy.** The study of spectra obtained by the passage of radiant energy from a continuous source through a cooler, selectively absorbing medium.

**Absorption Spectrum.** The array of absorption lines and absorption bands which results from the passage of radiant energy from a continuous source through a cooler, selectively absorbing medium.

**Absorption Tube.** A tube filled with a solid absorbent and used to absorb gases and vapors.

**Absorptive Power.** See absorptivity.

**Absorptivity.** The constant  $a$  in the Beer's law relation  $A=abc$ , where  $A$  is the absorbance,  $b$  the path length, and  $c$  the concentration of solution. Also known as absorptive power. Formerly known as absorbency index; absorption constant; extinction coefficient.

**Accelofilter.** A filtration device that uses a vacuum or pressure to draw or force the liquid through the filter to increase the rate of filtration.

**Acetanilide.** An odorless compound in the form of white, shining, crystalline leaflets or a white, crystalline powder with a melting point of 114—116°C; soluble in hot water, alcohol, ether, chloroform, acetone, glycerol, and benzene; used as a rubber accelerator, in the manufacture of dyestuffs and intermediates, as a precursor in penicillin manufacture, and as a painkiller. Also known as *N*-phenylacetamide.

**Acetoacetate.** A salt which contains the  $\text{CH}_3\text{COCH}_2\text{COO}$  radical; derived from acetoacetic acid.

**Acetolysis.** Decomposition of an organic molecule through the action of acetic acid or acetic anhydride.

**Acetone Number.** A ratio used to estimate the degree of polymerization of materials such as drying oils; it is the weight in grams of acetone added to 100 grams of a drying oil to cause an insoluble phase to form.

**Acetone-sodium Bisulfite**  $(\text{CH}_3)_2\text{C}(\text{OH})\text{SO}_3\text{Na}$ . Crystals that have a slight sulfur dioxide odor and slightly fatty feel; freely soluble in water, decomposed by acids; used in photography and in textile dyeing and printing. Also known as acetone sulfite; 2-hydroxy-2 propanesulfonic acid sodium salt; sodium-acetone bisulfite.

**Acetylating Agent.** A reagent, such as acetic anhydride, capable of bonding an acetyl group onto an organic molecule.

**Acetyllation.** The process of bonding an acetyl group onto an organic molecule.

**Acetyl Bromide**  $\text{CH}_3\text{COBr}$ . A colourless, fuming liquid with a boiling point of  $81^\circ\text{C}$ ; soluble in ether, chloroform, and benzene; used in organic synthesis and dye manufacture.

**Acetyl Chloride**  $\text{CH}_3\text{COCl}$ . A colourless, fuming liquid with a boiling point of  $51-52^\circ\text{C}$ ; soluble in ether, acetone, and acetic acid; used in organic synthesis, and in the manufacture of dyestuffs and pharmaceuticals. Also known as ethanoyl chloride.

**Acetyl Number.** A measure of free hydroxyl groups in fats or oils determined by the amount of potassium hydroxide used to neutralize the acetic acid formed by saponification of acetylated fat or oil.

**Acetyl Value.** The number of milligrams of potassium hydroxide required for neutralization of acetic acid obtained by the saponification of one gram of acetylated fat or oil sample. Acetylation is carried out by boiling the sample with an equal amount of acetic anhydride, washing and drying. Saponification values on the acetylated and on untreated fat are determined. From the results the acetyl value is calculated. It is a measure of the number of free hydroxyl groups in the fat or oil.

**Achromatic Indicators.** Substances which give a grey end-point and generally find application in the titration of turbid liquids.

**Acid-base Equilibrium.** The condition when acidic and basic ions in a solution exactly neutralize each other; that is, the pH is 7.

**Acid-base Indicator.** A substance, a weak acid or weak base, which has a different colour in acid or base solution. The colour change is due to a marked difference in colour between the undissociated and ionic forms. For a good indicator the colour change must occur between narrow limits of pH, e.g. methyl orange is red at pH 3.1 and change to yellow at pH 4.4.

**Acid Calcium Phosphate.** See calcium phosphate.

**Acid Cell.** An electrolytic cell whose electrolyte is an acid.

**Acid Chloride.** A compound containing the radical  $\text{-COCl}$ ; an example is benzoyl chloride.

**Acid Conductor.** A vessel designed for refortification of hydrolyzed acid by heating and evaporation of water, or sometimes by distillation of water under partial vacuum.

**Acid Dye.** Any of a group of sodium salts of sulfonic and carboxylic acids used to dye natural and synthetic fibres, leather, and paper.

**Acid Heat Test.** The determination of degree of unsaturation of organic compounds by reacting with sulfuric acid and measuring the heat of reaction.

**Acidic Titrant.** An acid solution of known concentration used to determine the basicity of another solution by titration.

**Acidification.** Addition of an acid to a solution until the pH falls below 7.

**Acidimeter.** An apparatus or a standard solution used to determine the amount of acid in a sample.

**Acidimetry.** The titration of an acid with a standard solution of base.

**Acidity.** The state of being acid.

**Acidity Coefficient.** The ratio of the oxygen content of the bases in a rock to the oxygen content in the silica.- Also known as oxygen ratio.

**Acid Number.** See acid value.

**Acidolysis.** A chemical reaction involving the decomposition of a molecule, with the addition of the elements of an acid to the molecule; the reaction is comparable to hydrolysis or alcoholysis, in which water or alcohol, respectively, is used in place of the acid. Also known as acyl exchange.

**Acid Value.** The number of milligrams of potassium hydroxide required to neutralize the free acids present in one gram of oil, fat, or wax. The determination is made by titrating the sample in hot 95% ethyl alcohol using phenolphthalein as indicator.

**Acidimetry.** The determination of the concentration of acid solutions or of the quantity of acid in a sample or mixture. This is usually done by titration with a solution of base of known strength (standard solution); an indicator is used to establish the end point.

**Acree's Reaction.** A test for protein in which a violet ring appears when concentrated sulfuric acid is introduced below a mixture of the unknown solution and a formaldehyde solution containing a trace of ferric chloride.

**Acridine Orange.** A dye with an affinity for nucleic acids; the complexes of nucleic acid and dye fluoresce orange with RNA and green with DNA when observed in the fluorescence microscope.

**Acrolein Test.** A test for the presence of glycerin or fats; a sample is heated with potassium bisulfate, and acrolein is released if the test is positive.

**Action chemistry.** A branch of chemistry concerned with chemical reactions produced by light or other radiation.

**Activated Complex.** An energetically excited state which is intermediate between reactants and products in a chemical reaction.

**Activation.** Treatment of a substance, by heat, radiation, or activating reagent to produce a more complete or rapid chemical or physical change.

**Activation Analysis.** An analytical technique in which an artificial radioactive isotope is formed by irradiation (generally with neutrons) from the stable element to be determined and the amount of the artificial isotope is then estimated from its radioactivity.

**Activation Energy.** The energy, in excess over the ground state, which must be added to an atomic or molecular system to allow a particular process to take place.

**Addition Reaction.** A type of reaction of unsaturated hydrocarbons with hydrogen, halogens, halogen acids, and other reagents, so that no change in valency is observed and the organic compound forms a more complex one.

**Adiabatic Calorimeter.** An instrument used to study chemical reactions which have a minimum loss of heat.

**Adiabatic Flame Temperature.** The highest possible temperature of combustion obtained under the conditions that the burning occurs in an adiabatic vessel, that it is complete, and that dissociation does not occur.

**Adsorbate.** A solid, liquid, or gas which is adsorbed as molecules, atoms, or ions by such substances as charcoal, silica, metals, water and mercury.

**Adsorbent.** A solid or liquid that adsorbs other substances; for example, charcoal, silica, metals, water, and mercury.



**Adsorption.** The surface retention of solid, liquid, or gas molecules, atoms, or ions by a solid or liquid, as opposed to absorption, the penetration of substances into the bulk of the solid or liquid.

**Adsorption Chromatography.** Separation of a chemical mixture (gas or liquid) by passing it, over an adsorbent bed which adsorbs different compounds at different rates.

**Adsorption Indicator.** An indicate which functions by adsorption on the surface of a precipitate. Thus in precipitating  $\text{AgCl}$  in the presence of excess  $\text{Cl}^-$  the surface has a layer of  $\text{Cl}^-$  and is negatively charged; in the presence of the indicator fluorescein the indicator is in solution. As soon as there is excess of  $\text{Ag}^+$  the precipitate takes on a positive charge and the presence of the fluorescein anion as counter ion gives the precipitate a pinked red colour.

**Adsorption Isobar.** A graph showing how adsorption varies with some parameter, such as temperature, while holding pressure constant.

**Adsorption Isotherm.** The relationship between the gas pressure  $p$  and the amount  $w$ , in grams, of a gas or vapor taken up per gram of solid at a constant temperature.

**AES.** Auger electron spectroscopy.

**Affinity Chromatography.** A chromatographic technique that utilizes the ability of biological molecules to bend to certain ligands specifically and reversibly; used in protein biochemistry.

**Aggressive Carbon Dioxide.** The carbon dioxide dissolved in water in excess of the amount required to precipitate a specified concentration of calcium ions as calcium carbonate; used as a measure of the corrosivity and scaling properties of water.

**Air Line.** Lines in a spectrum due to the excitation of air molecules by spark discharges, and not ordinarily present in arc discharges.

**Air Shower.** See cosmic-ray shower.

**Albite Law.** A rule specifying the orientation of alternating lamellae in multiple twin feldspar crystals; the twinning plane is brachypinacoid and is common in albite.

**Alignment.** A population  $p(m)$  of the  $2I+1$  orientational substates of a nucleus;  $m = -I$  to  $+I$ , such that  $p(m) = p(-m)$ .

**Alkaescence.** The property of a substance that is alkaline, that is, having a pH greater than 7.

**Alkali.** A hydroxide of one of the alkali metals. Also used for such substances as  $\text{CaO}$ ,  $\text{Ca(OH)}_2$ ,  $\text{Na}_2\text{CO}_3$ , which give an alkaline solution ( $\text{pH} < 7$ ) in water. In aqueous solution the term alkali is virtually synonymous with the term base.

**Alkali Blue.** The sodium salt of triphenylrosanilinesulfonic acid; used as an indicator.

**Alkalimeter.**

1. An apparatus for measuring the quantity of alkali in a solid or liquid.
2. An apparatus for measuring the quantity of carbon dioxide formed in a reaction.

**Alkalimetry.** Quantitative measurement of the concentration of bases or the quantity of one free base in a solution; techniques include titration and other analytical methods.

**Alkaline**

1. Having properties of an alkali.
2. Having a pH greater than 7.

**Alkaloid Reagents.** Reagents, most of which are acids with complex anions, which give precipitates with alkaloids. The alkaloid reagents include chloroplatinic, phosphotungstic, phosphomolybdic, cyanoferrate, tannic, picric and sulphosalicylic acids, and potassium iodoiodomercurate(II). They also precipitate proteins.

methods. The physical methods most used are ultraviolet, infrared, or nuclear magnetic resonance spectroscopy, mass spectrometry, or molecular weight determination. Chromatography is much used.

Quantitative analysis is the estimation of the amount of element or group present in a mixture or compound. This is done by various methods, in volumetric analysis a titration, in gravimetric analysis a precipitation followed by a weighing, in colorimetric analysis the estimation of a coloured species. Other quantitative methods include infrared spectroscopy, estimation of the opalescence of a precipitate (turbidimetry, nephelometry and fluorimetry), estimation of optical rotation, electrolytic decomposition, potentiometric, conductometric and amperometric titrations, and polarography. Using the appropriate methods analysis can be carried out on almost any quantity of material. Organic quantitative analysis is generally carried out by physical methods or by conversion to known derivatives which can be estimated by weighing or by titration.

**Analytical Chemistry.** The subdivision of chemistry concerned with identification of materials (qualitative analysis) and with determination of the percentage composition of mixtures or the constituents of a pure compound (quantitative analysis). The gravimetric and volumetric (or "wet") methods (precipitation, titration, and solvent extraction) are still used for routine work; indeed, new titration methods have been introduced, e.g., cryoscopic, pressure metric (for reactions that produce a gaseous product), redox methods, and use of a fluoride-sensitive electrode. However, faster and more accurate techniques (collectively called instrumental) have been developed in the last few decades. Among these are infrared, ultraviolet, and x-ray spectroscopy, where the presence and amount of a metallic element is indicated by lines in its emission or absorption spectrum; colorimetry, by which the percentage of a

substance in solution is determined by the intensity of its colour; chromatography of various types by which the components of a liquid or gaseous mixture are determined by passing it through a column of porous material, or on thin layers of finely divided solids; separation of mixtures in ion-exchange columns; and radioactive tracer analysis. Optical and electron microscopy, mass spectrometry, microanalysis, nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) spectroscopy all fall within the area of analytical chemistry. See also spectroscopy, nuclear magnetic resonance, NQR spectroscopy, chromatography.

**Analysis.** The determination of the composition of a substance.

**Analyte.** The sample being analyzed.

**Analytical Chemistry.** The branch of chemistry dealing with techniques which yield any type of information about chemical systems.

**Analytical Distillation.** Precise resolution of a volatile liquid mixture into its components; the mixture is vaporized by heat or vacuum, and the vaporized components are recondensed into liquids at their respective boiling points.

**Analytical Extraction.** Precise transfer of one or more components of a mixture (liquid to liquid, gas to liquid, solid to liquid) by contacting the mixture with a solvent in which the component of interest is preferentially soluble.

**Analyzing Power.** In a nuclear scattering process, a measure of the effect on scattering cross sections of changes in the polarization of the beam or target nuclei.

**Andrews Titration.** An important titration for the estimation of reducing agents. The reducing agent is dissolved in concentrated hydrochloric acid and titrated with potassium iodate(V) solution. A drop of carbon tetrachloride is added to the solution and the end point is indicated by the disappearance of the iodine colour from this layer. The reducing agent is

oxidized and the iodate reduced to  $\text{ICl}$ , i.e. a 4-electron change.

**Anemometer.** Any instrument for measurement of gas velocity but normally referring to the instruments described below.

The vane anemometer consists of a small windmill mounted on jewelled bearings and attached to a revolution counter. In a stream of gas the rate of revolution of the windmill measures the gas velocity.

The hot-wire anemometer comprises an electrically heated wire placed in the gas stream. The rate of heat loss, and hence electrical resistance, is a function of gas velocity.

Low fluid velocities can be measured using thermistor anemometers.

**Angle-resolved Photoelectron Spectroscopy.** A type of photoelectron spectroscopy which measures the kinetic energies of photoelectrons emitted from a solid surface and the angles at which they are emitted relative to the surface. Abbreviated ARPES.

**Aniline Point.** The minimum temperature for a complete mixing of aniline and materials such as gasoline; used in some specifications to indicate the aromatic content of oils and to calculate approximate heat of combustion.

**Anion Exchange.** A type of ion exchange in which the immobilized functional groups on the solid resin are positive.

**Anisole  $\text{C}_6\text{H}_5\text{OCH}_3$ .** A colourless liquid that is soluble in ether and alcohol, insoluble in water; boiling point is  $155^\circ\text{C}$ ; vapors are highly toxic; used as a solvent and in perfumery. Also known as methoxybenzene; methylphenyl ether.

**Anode.** The positive electrode of an electrolytic cell, to which negatively charged ions travel when an electric current is passed through the cell. Such anodes are usually made of graphite or other form of carbon, though titanium has been successfully

introduced in the chlor-alkali industry. In a primary cell (battery or fuel cell) the anode is the negative electrode.

**Anode Corrosion Efficiency.** The ratio of actual weight loss of an anode due to corrosion to the theoretical loss as calculated by Faraday's law.

**Anode Effect.** A condition produced by polarization of the anode in the electrolysis of fused salts and characterized by a sudden increase in voltage and a corresponding decrease in amperage.

**Anode Film.** The portion of solution in immediate contact with the anode.

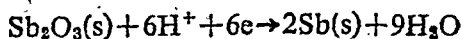
**Anodic Polarization.** The change in potential of an anode caused by current flow.

**Anolyte.** The part of the electrolyte at or near the anode that is changed in composition by the reactions at the anode.

**Anomalous Zeeman Effect.** A type of splitting of spectral lines of a light source in a magnetic field which occurs for any line arising from a combination of terms of multiplicity greater than one; due to a nonclassical magnetic behaviour of the electron spin.

**Antimonous Sulfide.** See antimony trisulfide.

**Antimony Electrode.** An electrode constructed from high purity antimony surface coated with a thin film of oxide. The half cell is



It is robust electrode but is not particularly accurate in use. Use in pH measurement.

**Antimonyl Potassium Tartrate.** See tartar emetic.

**Antimony Trisulfide  $Sb_2S_3$ .** Black and orange-red rhombic crystals; soluble in concentrated hydrochloric acid and sulfide solutions, insoluble in water; melting point  $546^\circ C$ ; used as a pigment, and in matches and pyrotechnics. Also known as antimonous

sulfide; antimony black; antimony needless; antimony orange; antimony sulfide; black antimony.

**Anti-stokes Lines.** Lines of radiated frequencies which are higher than the frequency of the exciting incident light.

**API Gravity.** A scale derived from the Baume scale and introduced by the American Petroleum Institute to express the gravity of oils.

$$\begin{aligned} ^\circ\text{API} &= \frac{141.5}{\text{sp. gr. } 60/60^\circ\text{F}} - 131.5 \\ &= \frac{141.36}{\text{density}/60^\circ\text{F}} - 131.5 \end{aligned}$$

(For sp. gr. also use relative density.)

**API Gravity.** A scale of measurement adopted by the American Petroleum Institute. It runs from 0.0 (equivalent to specific gravity 1.076) to 100.0 (equivalent to specific gravity 0.6112). The API values as used in the petroleum industry decrease as specific gravity values increase.

**API Scale.** The American Petroleum Institute hydrometer scale for the measurement of the specific gravity of liquids; used primarily in the American petroleum industry.

**Aprotic Solvent.** A solvent that does not yield or accept a proton.

**Aquametry.** Analytical processes to measure the water present in materials; methods include Karl Fischer titration, reactions with acid chlorides and anhydrides, oven drying, distillation, and chromatography.

**Aqua Regia.** A fuming, highly corrosive, volatile liquid with a suffocating odor made by mixing 1 part concentrated nitric acid and 3 parts concentrated hydrochloric acid; reacts with all metals, including silver and gold. Also known as chloroazotic acid; chloronitrous acid; nitrohydrochloric acid; nitromuriatic acid.

(AOC-1)

**Aqueous Solution.** A solution with the solvent as water.

**Aquo Ion.** Any ion containing one or more water molecules.

**Arc Excitation.** Used of electric-arc energy to move electrons into higher energy orbits.

**Archeological Chemistry.** Application of the techniques of analytical chemistry to identification of materials found in excavations. Among those used are microanalytical methods, spectroscopic analysis, x-rays, and other types of nondestructive tests. For age determination, C-14 measurement (chemical dating) has been a valuable tool.

**Arc Spectrum.** The spectrum of a neutral atom, as opposed to that of a molecule or an ion; it is usually produced by vaporizing the substance in an electric arc; designated by the roman numeral I following the symbol for the element, for example, HeI.

**Argentometry.** A volumetric analysis that employs precipitation of insoluble silver salts; the salts may be chromates or chlorides.

**Aroylation.** A reaction in which the aroyl group is incorporated into a molecule by substitution.

**ARPES.** Angle-resolved Photoelectron Spectroscopy.

**Ascending Chromatography.** A technique for the analysis of mixtures of two or more compounds in which the mobile phase (sample and carrier) rises through the fixed phase.

**Ash.** In analytical chemistry, the residue remaining after complete combustion of a material; it consists of mineral matter (silica, alumina, iron oxide, etc. the amount often being a specification requirement.

**Ashing.** An analytical process in which the chemical material being analyzed is oven-heated to leave only noncombustible ash.



**ASTM Gum Test**

1. Determination of the amount of existing gum in a gasoline by evaporating a sample from a glass dish or an elevated temperature bath with the aid of circulating air.
2. Any gum test carried out in accordance with an ASTM gum test procedure.

**ASTM Melting Point.** The temperature at which wax first shows a minimum rate of temperature change.

**Astrochemistry.** Application of radioastronomy (micro-wave spectroscopy) to determination of the existence of chemical entities in the gas clouds of interstellar space and of elements and compounds in celestial bodies, including their atmospheres. Such data have been obtained from spectrographic study of the light from the sun and stars, from analysis of meteorites, and from actual samples from the moon. Hydrogen is by far the most abundant element in interstellar space, with helium a distant second. Over 25% of the elements, including carbon, have been identified, as well as molecules of water, carbon monoxide, carbon dioxide, ammonia, ethane, methane, acetylene, formaldehyde, formic acid, methyl alcohol, hydrogen cyanide, and acetonitrile. When applied to the planets only, the science is called chemical planetology.

**Astronomical Spectrograph.** An instrument used to photograph spectra of stars.

**Astronomical Spectroscopy.** The use of spectrographs in conjunction with telescopes to obtain observational data on the velocities and physical conditions of astronomical objects.

**Asymmetric Synthesis.** Chemical synthesis of a pure enantiomer, or of an enantiomorphous mixture in which one enantiomer predominates, without the use of resolution.

**Atmospheric Distillation** Distillation operation conducted at atmospheric pressure, in contrast to vacuum distillation or pressure distillation.

**Atomic Absorption Spectroscopy.** An analytical technique in which characteristic radiation is absorbed by non-excited atoms in the vapour state. The sample is volatilized with a burner.

**Atomic Emission Spectroscopy.** An analytical technique used for the determination of trace metals. The sample is vaporized and excited in an arc or flame and the emission spectra observed.

**Atomic Energy Level.** A definite value of energy possible for an atom, either in the ground state or an excited condition.

**Atomic Ground State.** The state of lowest energy in which an atom can exist. Also known as atomic unexcited state.

**Atomic Hydrogen.** Gaseous hydrogen whose molecules are dissociated into atoms.

**Atomic Magnet.** An atom which possesses a magnetic moment either in the ground state or in an excited state.

**Atomic Magnetic Moment.** A magnetic moment, permanent or temporary, associated with an atom, measured in magnetons.

**Atomic Polarization.** Polarization of a material arising from the change in dipole moment accompanying the stretching of chemical bonds between unlike atoms in molecules.

**Atomic Spectroscopy.** The branch of physics concerned with the production, measurement, and interpretation of spectra arising from either emission or absorption of electromagnetic radiation by atoms.

**Atomic Spectrum.** The spectrum of radiations due to transitions between energy levels in an atom, either absorption or emission.

**Atomic Vibration.** Periodic, nearly harmonic changes in position of the atoms in a molecule giving rise to many properties of matter, including molecular spectra, heat capacity, and heat conduction.

**Azoic Dye.** A water-insoluble azo dye that is formed by coupling of the components on a fibre. Also known as ice color; ingrain color.

**Azotometer.** See nitrometer.

## B

**Babcock Test.** A rapid test for butterfat in milk introduced by Stephen M. Babcock in 1890 and now in world-wide use in the dairy industry.

**Babo's Law.** A law stating that the relative lowering of a solvent's vapour pressure by a solute in the same at all temperatures.

**Backbending.** A discontinuity in the rotational levels of some rare-earth nuclei around spin 20 (where the same character is Planck's constant divided by  $2\pi$ ), which appears as a backbend on a graph that plots the moment of inertia versus the square of the rotational frequency.

**Back-reflection Photography.** A method of studying crystalline structure by x-ray diffraction in which the photographic film is placed between the source of x-rays and the crystal specimen.

**Back Titration.** A titration to return to the end point which was passed.

**Badger's Rule.** An empirical relationship between the stretching force constant for a molecular bond and the bond length.

## Balance

- (1) Exact equality of the number of atoms of various elements entering into a chemical reaction and the number of atoms of those elements in the reaction products. For example, in the reaction  $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ , the atoms in the input side are hydrogen 2, sodium 1, oxygen 1, and chlorine 1; each of these is also present in the products, though in different combination. The atoms of catalysts (when present) do not enter into reactions, and therefore are not involved. The balance of chemical reactions follows the law of conservation of mass. The term "material balance" is used by chemical engineers in designing processing equipment; it denotes a precise list of all the substances to be introduced into reaction and all those that will leave it in a given time, the two sums being equal.
- (2) A precision instrument designed for weighing extremely small amounts of the material with high accuracy. An analytical balance, or microbalance, for weights from about 1 gram to 0.1 milligram, is standard equipment in chemical laboratories. Its essential feature is a one-piece metal beam (lever) pivoted on a knife-edge or flexure at its exact center (fulcrum), so that it is free to oscillate. From it are suspended to scale pans about 2 in. in diameter, each of which is also positioned on a knife-edge on the lower arms of the beam. Exact balance is indicated by a pointer attached to the beam. Either an aluminium rider or a chain and vernier is provided for maximum accuracy. Highly sophisticated balances operating electronically with built-in micro-processors have become available in recent years.

An accurate laboratory balance weighs to the nearest hundredth of a milligram. Specially designed balance can be accurate to a million of a milligram. More modern substitution

balances use the substitution principle. In this calibrated weights are removed from the single lever arm to bring the single pan suspended from it into equilibrium with a fixed counter weight. The substitution balance is more accurate than the two-pan device and enables weighing to be carried out more rapidly. In automatic electronic balances, mass is determined not by mechanical deflection but by electronically controlled compensation of an electric force. A scanner monitors the displacement of the pan support generating a current proportional to the displacement. This current flows through a coil forcing the pan support to return to its original position by means of a magnetic force. The signal generated enables the mass to be read from a digital display. The mass of the empty container can be stored in the balance's computer memory and automatically deducted from the mass of the container plus its contents.

**Balmer Lines.** Lines in the hydrogen spectrum, produced by transitions between  $n=2$  and  $n>2$  levels either in emission or absorption; here  $n$  is the principal quantum number.

**Balmer Series.** The set of Balmer lines.

### **Band**

1. The position and spread of a solute within a series of tubes in a liquid-liquid extraction procedure. Also known as zone.
2. See band spectrum.

**Band Head.** A location on the spectrogram of a molecule at which the lines of a band pile up.

**Band Spectrum.** A spectrum consisting of groups or bands of closely spaced lines in emission or absorption, characteristic of molecular gases and chemical compounds. Also known as band.

**Barfoed's Test.** A test for monosaccharides conducted in an acid solution; cupric acetate is reduced to cuprous oxide, a red precipitate.

**Barker Method.** A method utilizing a number of convenient rules which allow two observers to choose the same reference system to describe the same noncubic crystal.

**Barkometer.** A hydrometer calibrated to test the strength of tanning liquors used in tanning leather.

**Bariow's Rule.** The rule that the volume occupied by the atoms in a given molecule is proportional to the valences of the atoms, using the lowest valency values.

**Barn.** A unit of area equal to  $10^{-28}$  square centimeter; used in specifying nuclear cross sections.

**Barrels Per Calendar Day.** A unit measuring the average rate of oil processing in a petroleum refinery, with allowances for downtime over a period of time. Abbreviated BCD.

**Barrier Separation.** The separation of a two-component gaseous mixture by selective diffusion of one component through a separative barrier (microporous metal or nonporous polymeric).

**Bartlett Force.** A force between nucleons in which spin is exchanged.

**Baryta Water.** A solution of barium hydroxide.

**Basal Cleavage.** Cleavage parallel to the base of the crystal structure or to the lattice plane which is normal to one of the lattice axes.

**Basal Orientation.** A crystal orientation in which the surface is parallel to the base of the lattice or to the lattice plane which is normal to one of the lattice axes.

## Base

1. Any chemical species, ionic or molecular, capable of accepting or receiving a proton (hydrogen ion) from another substance; the other substance acts as an acid in giving of the proton; the hydroxyl ion is a base.

2. The primary substance in solution in crude oil, and remaining after distillation.

**Base Exchange.** An old term used to describe the capacity of soils, zeolites, clays, etc. to exchange their cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) for an equivalent of other cations without undergoing structural change. An example of the general process of ion exchange.

**Base-line Technique.** A method for measurement of absorption peaks for quantitative analysis of chemical compounds in which a base line is drawn tangent to the spectrum background; the distance from the base line to the absorption peak is the absorbence due to the sample under study.

**Base Metal.** Any of the metals on the lower end of the electrochemical series.

**Batch Distillation.** Distillation where the entire batch of liquid feed is placed into the still at the beginning of the operation, in contrast to continuous distillation, where liquid is fed continuously into the still.

**Batch Rectification** Batch distillation in which the boiled-off vapor is re-condensed into liquid form and refluxed back into the still to make contact with the rising vapours.

**Bathochromatic Shift.** The shift of the fluorescence of a compound toward the red part of the spectrum due to the presence of a bathochrome radical in the molecule.

**Battery.** An electrochemical device that generates electric current by converting chemical energy to electrical energy. Its essential components are positive and negative electrodes made of more or less electrically conductive materials, a separating medium, and an electrolyte. There are four major types :

- (1) primary batteries (dry cells), which are not reversible and in which the anode (zinc) is the negative plate, and the cathode (graphite) is the positive plate, with ammonium chloride as electrolyte;

2. secondary or storage batteries, which are reversible and can be recharged, and in which lead sponge is the negative plate (anode) and lead oxide the positive plate (cathode), with sulfuric acid as electrolyte;
3. nuclear and solar cells, or energy converters; and
4. fuel cells. So-called superbatteries of high charge density have been developed using solid electrolytes of lithium-titanium dioxide and trilithium nitride, in which Li atoms are intercalated in the crystal structure. For further information see dry cell; storage battery; voltaic cell; fuel cell; solar cell; intercalation.

**Battery Electrolyte.** A liquid, paste, or other conducting medium in a battery, in which the flow of electric current takes place by migration of ions.

**Baume Hydrometer Scale.** A calibration scale for liquids that is reducible to specific gravity by the following formulas: for liquids heavier than water,  $\text{specific gravity} = 145 \div (145 - n)$  (at 60°F); for liquids lighter than water,  $\text{specific gravity} = 140 \div (130 + n)$  at 60°F;  $n$  is the reading on the Baume scale, in degrees Baume. Baume is abbreviated Be.

**Bead Test.** In mineral identification, a test in which borax is fused to a transparent bead, by heating in a blowpipe flame, in a small loop formed by platinum wire; when suitable minerals are melted in this bead, characteristic glassy colours are produced in an oxidizing or reducing flame and serve to identify elements.

**Beam Attenuator.** An attachment to the spectrophotometer that reduces reference to beam energy to accommodate undersized chemical samples.

**Beam-condensing Unit.** An attachment to the spectrophotometer that condenses and remagnifies the beam to provide reduced radiation at the sample.



**Beam-foil Spectroscopy.** A method of studying the structure of atoms and ions in which a beam of ions energized in a particle accelerator passes through a thin carbon foil from which the ions emerge with various numbers of electrons removed and in various excited energy levels; the light on Auger electrons emitted in the deexcitation of these levels are then observed by various spectroscopic techniques, Abbreviated BFS.

**Bed.** The ion-exchange resin contained in the column in an ion-exchange system.

**Beer-lambert-bouguer Law.** See Bouguer-Lambert-Beer law.

**Beer's Law.** The law which states that the absorption of light by a solution changes exponentially with the concentration, all else remaining the same.

**Benedict's Solution.** A solution of potassium and sodium tartrates, copper sulfate, and sodium carbonate; used to detect reducing sugars.

**Benedict's Test.** A biochemical test to detect reducing sugars in solution, devised by the US chemist S. R. Benedict (1884-1939). Benedict's reagent—a mixture of copper(II) sulphate and a filtered mixture of hydrated sodium citrate and hydrated sodium carbonate—is added to the test solution and boiled. A high concentration of reducing sugars induces the formation of a red precipitate; a lower concentration produces a yellow precipitate. Benedict's test is a more sensitive alternative to Fehling's test.

**Benzol-acetone Process.** A solvent dewaxing process in which a mixture of the solvent and oil containing wax is cooled until the wax solidifies and is then removed by filtration.

**Berthelot Equation.** A form of the equation of state which relates the temperature, pressure, and volume of a gas with the gas constant.

**Berthelot-thomsen Principle.** The principle that of all chemical reactions possible, the one developing the greatest amount of heat will take place, with certain obvious exceptions such as changes of state.

**Berthollide.** A compound whose solid phase exhibits a range of composition.

**Beta Decay Spectrum.** The distribution in energy or momentum of the beta particles arising from a nuclear disintegration process.

**Beta-ray Spectrometer.** An instrument used to determine the energy distribution of beta particles and secondary electrons. Also known as beta spectrometer.

**Beta Spectrometer.** See beta-ray spectrometer.

**Biamperometry.** Amperometric titration that uses two polarizing or indicating electrodes to detect the end point of a redox reaction between the substance being titrated and the titrant.

**Biaxial Crystal.** A crystal of low symmetry in which the index ellipsoid has three unequal axes.

**Biaxial Indicatrix.** An ellipsoid whose three axes at right angles to each other are proportional to the refractive indices of a biaxial crystal.

**Bimolecular Reaction.** A chemical transformation or change involving two molecules.

**Binary Encounter Approximation.** An approximation for predicting the probability that an incident proton will eject an inner shell electron from an atom; it uses a semiclassical treatment of momentum transfer from the incident proton to the ejected electron.

**Binary Separation.** Separation by distillation or solvent extraction of a fully miscible liquid mixture of two chemical compounds.

**Bioassay.** A method for quantitatively determining the concentration of a substance by its effect on the growth of a suitable animal, plant, or microorganism under controlled conditions.

**Bioautography.** A bioassay based upon the ability of some compounds (for example, vitamin B<sub>12</sub>) to enhance the growth of some organism or compounds and to repress the growth of others; used to assay certain antibiotics.

**Biochemical Oxygen Demand (B.O.D.).** A standardized means of estimating the degree of contamination of water supplies, especially those which receive contamination from sewage and industrial wastes. (See also sewage sludge, biodegradability). It is expressed as the quantity of dissolved oxygen (in mg/liter) required during stabilization of the decomposable organic matter by aerobic biochemical action. Determination of this quantity is accomplished by diluting suitable portions of the sample with water saturated with oxygen and measuring the dissolved oxygen in the mixture both immediately and after a period of incubation, usually five days. See also dissolved oxygen (D.O.) and oxygen consumed (C.O.D.) as related terms.

**Biochemorhology.** The science dealing with the chemical structure of foods and drugs and their reactions on living organisms.

**Biogeochemical Prospecting.** A prospecting technique for subsurface ore deposits based on interpretation of the growth of certain plants which reflect subsoil concentrations of some elements.

**Biogeochemistry.** A branch of geochemistry dealing with the interactions between living organisms and their mineral environment. It includes among other studies that of the effect of plants on weathering of rocks; of the chemical transformations that produced petroleum and coal; of the concentration of specific elements in vegetation at some time in the geochemical cycle (iodine in sea plants, uranium in some forms of decaying organic matter); and of the organic constituents of fossils.

**Bismuth Subnitrate**  $4\text{BiNO}_3(\text{OH})_2 \cdot \text{BiO}(\text{OH})$ . A white, hygroscopic powder. Also known as basic bismuth nitrate.

**Biuret  $\text{NH}_2\text{CONHCONH}_2$ .** Colorless needles that are soluble in hot water and decompose at  $190^\circ\text{C}$ ; a condensation product of urea. Also known as allophanamide; carbamylurea; dicarbamylamine.

**Biuret Test.** A biochemical test to detect proteins in solution, named after the substance biuret ( $\text{H}_2\text{NCONHCONH}_2$ ), which is formed when urea is heated. Sodium hydroxide is mixed with the test solution and drops of 1% copper(II) sulphate solution are then added slowly. A positive result is indicated by a violet ring, caused by the reaction of peptide bonds in the proteins or peptides. Such a result will not occur in the presence of free amino acids.

**Blocked Operation.** The use of a single chemical or refinery process unit alternately in more than one operation; for example, a catalytic reactor will first produce a chemical product and then will be blocked from the main process stream during catalyst regeneration.

**Blowpipe Reaction Analysis.** A method of analysis in which a blowpipe is used to heat and decompose a compound or mineral; characteristic color appears in the flame or a colored crust appears on charcoal.

**Blue Tetrazolium.**  $\text{C}_{40}\text{H}_{52}\text{Cl}_2\text{N}_8\text{O}_2$  Lemon yellow crystals that decompose at  $242\text{--}246^\circ\text{C}$ ; soluble in chloroform, ethanol, and methanol; used in seed germination research, as a stain for molds and bacteria, and in histochemical studies. Also known as dimethoxy neotetrazolium; ditetrazolium chloride; tetrazolium blue.

**Boettger's Test.** A test for the presence of saccharides, utilizing the reduction of bismuth subnitrate to metallic bismuth, a precipitate.

**Bohr Atom.** An atomic model having the structure postulated in the Bohr theory.

**Bohr Effect.** The effect of carbon dioxide and pH on the oxygen equilibrium of hemoglobin; increase in carbon dioxide prevents an increase in the release of oxygen from oxyhemoglobin.

**Bohr Magneton.** The amount  $he/4\pi mc$  of magnetic moment, where,  $h$  is Planck's constant,  $e$  and  $m$  are the charge and mass of the electron, and  $c$  is the speed of light.

**Bohr Orbit.** One of the electron paths about the nucleus in Bohr's model of the hydrogen atom.

**Bohr Radius.** The radius of the ground-state orbit of the hydrogen atom in the Bohr theory.

**Bohr-Sommerfeld Theory.** A modification of the Bohr theory in which elliptical as well as circular orbits are allowed.

**Bohr Theory.** A theory of atomic structure postulating an electron moving in one of certain discrete circular orbits about a nucleus with emission or absorption of electromagnetic radiation necessarily accompanied by transitions of the electron between the allowed orbits.

**Boiling Point.** The temperature of a liquid at which its vapor pressure is equal to or very slightly greater than the atmospheric pressure of the environment. For water at sea level it is  $212^{\circ}\text{F}$  ( $100^{\circ}\text{C}$ ).

**Bomb.** A small metal container containing gases or liquids under varying degrees of pressure. An aerosol bomb usually contains insecticides which are emitted as an atomized spray on release of pressure, the gases used being carbon dioxide, nitrous oxide, butane, etc., at relatively low pressure. An oxygen bomb is used for accelerated aging tests for rubber and plastic products; oxygen under high pressure is used. This device must be handled by a trained technician.

**Bonded-phase Chromatography.** A type of high-pressure liquid chromatography which employs a stable, chemically bonded stationary phase.

**Borax-bead Test.** A simple laboratory test for certain metal ions in salts. A small amount of the salt is mixed with borax and a molten bead formed on the end of a piece of platinum wire. Certain metals can be identified by the colour of the bead produced in the oxidizing and reducing parts of a Bunsen flame. For example, iron gives a bead that is red when hot and yellow when cold in the oxidizing flame and a green bead in the reducing flame.

**Born Equation.** An equation for determining the free energy of solvation of an ion in terms of the Avogadro number, the ionic valency, the ion's electronic charge, the dielectric constant of the electrolytic, and the ionic radius.

**Born-oppenheimer Method.** A method for calculating the force constants between atoms by assuming that the electron motion is so fast compared with the nuclear motions that the electrons follow the motions of the nuclei adiabatically.

**Bouguer-lambert-beer Law.** The intensity of a beam of monochromatic radiation in an absorbing medium decreases exponentially with penetration distance. Also known as Beer-Lambert-bouguer law ; Lambert-Beer law.

**Bouguer-lambert Law.** The law that the change in intensity of light transmitted through an absorbing substance is related exponentially to the thickness of the absorbing medium and a constant which depends on the sample and the wavelength of the light. Also known as Lambert's law.

**Boundary Line.** On a phase diagram, the line along which any two phase areas adjoin in a binary system, or the line along which any two liquidus surfaces intersect in a ternary system.

**Bouvealt-blanc Method.** A laboratory method for preparing alcohols by reduction of esters utilizing sodium dissolved in alcohol.

**Brackett Series.** A series of lines in the infrared spectrum of atomic hydrogen whose wave numbers are give by  $R_H [(1/16)-(1/n^2)]$ , where  $R_H$  is the Rydberg constant for hydrogen and  $n$  is any integer greater than 4.

**Brady's Reagent.** See 2,4-dinitrophenylhydrazine.

### **Bragg Curve**

1. A curve showing the average number of ions per unit distance along a beam of initially monoenergetic ionizing particles, usually alpha particles, passing through a gas. Also known as Bragg ionization curve.
2. A curve showing the average specific ionization of an ionizing particle of a particular kind as a function of its kinetic energy, velocity, or residual range.

**Bragg-Kleeman Rule.** See Bragg rule.

### **Branch**

1. A product resulting from one mode of decay of a radioactive nuclide that has two or more modes of decay.
2. A carbon side chain attached to a molecule's main carbon chain.

**Bravals Indices.** A modification of the Miller indices; frequently used for hexagonal and trigonal crystalline systems; they refer to four axes the  $c$ -axis and three others at  $120^\circ$  angles in the basal plane.

**Bravals Lattice.** One of the 14 possible arrangements of lattice points in space such that the arrangement of points about any chosen point is identical with that about any other point.

**Bright-line Spectrum.** An emission spectrum made up of bright lines on a dark background.

**Brix Degree.** A measure of the density or concentration of sugar solutions. The degrees Brix equals percent by weight of sucrose in the solution and is related empirically to the specific gravity

**Brix Scale.** A hydrometer scale for sugar solutions indicating the percentage by weight of sugar in the solution at a specified temperature.

**Broadening of Spectral Line.** A widening of spectral lines by collision or pressure broadening, or possible by Doppler effect.

**Bromocresol Green.** Tetrabromo-meta-cresolsulfon-phthalein, an acid base indicator, showing colour change from yellow to blue over the range pH 3.8-5.4. Yellow crystals; m.p. 218°C; slightly soluble in water, soluble in alcohol.

**Bromocresol Purple.** Dibromo-ortho-cresolsulfon-phthalein, an acid base indicator, changes from yellow to purple between pH 5.2-6.8. Yellow crystals; m.p. 241°C; insoluble in water, soluble in alcohol.

**Bromine Number.** The amount of bromine absorbed by a fatty oil; indicates the purity of the oil and degree of unsaturation.

**Bromine Test.** A laboratory test in which the unsaturated hydrocarbons present in a crude oil are determined by mixing a sample with bromine; the lower the rate of bromine absorption, the more paraffinic the test sample.

**Bromine Value.** An expression representing the number of centigrams of bromine absorbed by 1 gram of oil under test conditions; an indication of the degree of unsaturation of given oil.

**Bromine Water.** An aqueous saturated solution of bromine used as a reagent wherever a dilute solution of bromine is needed.

**Bromocresol Green.** Tetrabromo-m-cresol sulfonphthalein, a gray powder soluble in water or alcohol; used as an indicator between pH 4.5 (yellow) and 5.5 (blue). Also known as bromocresol green.

**Bromocresol Purple.** Dibromo-o-cresol sulfonphthalein, a yellow powder soluble in water; used as an indicator between pH 5.2 (yellow) and 6.8 (purple). Also known as bromocresol purple.



**Bromophenol Blue.** Tetrabromophenolsulfonphthalein, an acid-base indicator, showing colour change from yellow to purple over the range pH 3.0 to 4.6.

**n-Bromosuccinimide (NBS)**  $\text{CH}_2\text{CO})_2\text{NBr}$ . Properties : Fine crystals, white to cream in colour; melting range  $172\text{--}178^\circ\text{C}$  (decomposes). Soluble to carbon tetrachloride; 44.5% min. active bromine. Hazard : Respirators should be used in handling dry material, which evolves toxic fumes of bromine. Strong irritant to eyes and skin.

Use : For controlled low-energy bromination.

**Bromthymol Blue.**  $\text{C}_{27}\text{H}_{28}\text{Br}_2\text{O}_5\text{S}$ . Properties : Yellow-white crystals; soluble in alcohol and alkaline solutions; slightly soluble in water.

Uses : Indicator (yellow=pH 6.0; blue pH=7.6)

**Bromthymol Blue.** An acid-base indicator in the pH-range 6.0 to 7.6; colour change is yellow to blue. Also known as dibromothymolsulfonphthalein.

**Brown-ring Test.** A qualitative test used for the detection of nitrate. A freshly prepared solution of ferrous sulphate is mixed with the sample and concentrated sulphuric acid is introduced slowly to the bottom of the tube using a dropping pipette so that two layers are formed. A brown ring formed where the liquids meet indicates the presence of nitrate.

The brown colour is  $[\text{Fe}(\text{NO})]\text{SO}_4$ , which breaks down on shaking.

**Brunauer-emmett-teller Equation.** An extension of the Langmuir isotherm equation in the study of sorption; used for surface area determinations by computing the monolayer area. Abbreviated BET equation.

**Buchner Funnel.** A type of funnel with an internal perforated tray on which a flat circular filter paper can be placed, used for filtering by suction. It is named after the German chemist Eduard Buchner (1860—1917).

**Buffer.** A solution containing both a weak acid and its conjugate weak base whose pH changes only slightly on the addition of acid or alkali. The weak acid becomes a buffer when alkali is added, and the weak base becomes a buffer on addition of acid. This action is explained by the reaction



in which the base B is formed by the loss of a proton from the corresponding acid A. The acid may be a carbon such as  $NH_4^+$ , a neutral molecule such as  $CH_3COOH$ , or an anion such as  $H_2PO_4^-$ . When alkali is added, hydrogen ions are removed to form water; but, as long as the added alkali is not in excess of the buffer acid, many of the hydrogen ions are replaced by further ionization of A to maintain the equilibrium. When acid is added, this reaction is reversed as hydrogen ions combine with B to form A.

The pH of a buffer solution may be calculated by the mass law equation

$$pH = pK' + \log \frac{C_B}{C_A}$$

in which  $pK'$  is the negative logarithm of the apparent ionization constant of the buffer acid and the concentrations are those of the buffer base and its conjugate acid.

**Buffer Capacity.** The relative ability of a buffer solution to resist pH change upon addition of an acid or a base.

**Buffer Solution.** See buffer.

**Bunsen Burner.** A gas burner consisting of a vertical metal tube with an adjustable air-inlet hole at the bottom. Gas is allowed into the bottom of the tube and the gas-air mixture is burnt at the top. With too little air the flame is yellow and sooty. Correctly, adjusted, the burner gives a flame with a pale blue inner cone of incompletely burnt gas, and an almost invisible outer flame where the gas fully oxidized and reaches a temperature of about  $1500^\circ C$ .

**Bunsen-Kirchhoff Law.** The law that every element has a characteristic emission spectrum of bright lines and an absorption spectrum of dark lines.

**Buoyancy Balance.** A balance with a hollow silica bulb on one arm and a massive cylinder on the other. Used to measure the vapour density of the gas surrounding the bulb or by adjusting gas pressure to weigh. Can be sensitive to  $10^{-11}$ g.

**Burette.** Apparatus used for measuring the quantity of a liquid or gas in a chemical operation. In volumetric analysis the burette generally consists of a vertical tube, graduated in fractions of a millilitre, provided with a tap at the lower end, by means of which the amount of liquid which is allowed to flow from the graduated tube may be controlled. In more precise work, a weight burette is employed. It consists of a flat-bottomed flask provided with a ground stopper, and a narrow side limb provided with a ground glass cap. The burette is weighed before and after releasing the requisite amount of liquid from the narrow side-limb.

In gas analysis the burettes are generally vertical graduated tubes provided with a tap at the upper end. The lower end is connected by means of rubber tubing to a reservoir containing mercury or water, by means of which the pressure on the gas enclosed between the tap and the liquid surface may be adjusted and ascertained. This form of burette was devised by Hempel. The Bunte gas burette has an additional tap at the lower end.

**Burners.** For the combustion of solid, gaseous or liquid fuels on an industrial scale special burners are usually necessary. Many designs are available, the main one being described below.

**Solid fuels.** Large coal-fired equipment normally uses pulverized fuel blown into the combustion chamber by a blast of air, similar to oil droplets. This ensures that complete combustion is possible with a minimum of excess air and also that a large range of solid fuels may be utilized. High and medium

volatile matter fuels are generally burned with a short, turbulent flame while low volatile matter fuels are burned with a long flame.

**Liquid fuels.** Industrial burners for liquid fuels usually atomize the fuels in hot air so that droplets will evaporate during combustion. For more volatile fuels such as kerosine, vaporizing burners of various types are employed, usually for domestic purposes.

Atomization can be effected by mechanical means or by an atomizing fluid such as air or steam. In pressure jet burners oil at a pressure of 700—3500 kM/m<sup>2</sup> passes through a fine nozzle to give a hollow cone of droplets. The oil may have to be heated to reduce its viscosity below 100 Redwood seconds. Rotary cup burners employ a conical, rotating cup which ejects a fine mist of oil into the furnace by centrifugal force. Air is supplied through an annular ring surrounding the mouth of the cone and helps to form the droplets into a cone. Blast burners or twin-fluid burners operate at various pressures and usually rely for atomization on the shearing action of air or steam with in the burner assembly.

**Gaseous fuels.** Gas burners can be diffusion flame burners or pre-aerated burners. Diffusion flame burners may be relatively simple, with fuel gas burning at an orifice in the surrounding air which diffuses into the gas. These flames are normally luminous because of the incandescence or carbon particles produced by cracking of the fuel. Improved combustion can be obtained by having impinging jets of gas and air to create turbulence. Pre-aerated burners are designed so that gas and air are pre-mixed in the burner and emerge as a flammable mixture. Various pressures of gas and air are employed industrially although the best-known example of a low-pressure, aerated burner is the laboratory bunsen burner.

Care must be taken in gas burner design to avoid lift-off of the flame or flash-back of the flame into the burner tube.

**Burner.** A furnace where sulfur or sulfide ore are burned to produce sulfur dioxide and other gases.

**Burning Velocity.** The normal velocity of the region of combustion reaction (reaction zone) relative to nonturbulent unburned gas, in the combustion of a flammable mixture.

**Butyric Acid**  $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ . A colourless, combustible liquid with boiling point  $163.5^\circ\text{C}$  (757 mm Hg); soluble in water, alcohol, and ether; used in synthesis of flavors, in pharmaceuticals, and in emulsifying agents. Also known as butanoic acid; n-butyric acid; ethyl acetic acid; propylformic acid.

## C

**Cabannes' Factor.** An equational factor to correct for the depolarization effect of the horizontal components of scattered light during the determination of molecular weight by optical methods.

**Cailletet and Mathias Law.** The law that describes the relationship between the mean density of a liquid and its saturated vapour at that temperature as being a linear function of the temperature.

**Calcium Fluoride**  $\text{CaF}_2$ . Colourless, cubic crystals that are slightly soluble in water and soluble in ammonium salt solutions.

**Calculated Cetane Index (CCI).** An indication of the ignition quality of diesel engine fuel by laboratory examination. CCI is obtained, usually from a nomograph, by a relationship between CCI, API gravity and the mid-boiling point temperature (F) recorded

by ASTM distillation. This index approximates to cetane number but the method is not applicable to fuels containing ignition quality improvers.

**Calgon.** Sodium metaphosphate used as a washing powder and cleansing agent.

**Caliche.** Impure sodium nitrate.

**Calibration Reference.** Any of the standards of various types that indicate whether an analytical instrument or procedure is working within prescribed limits; examples are test solutions used with pH meters, and solutions with known concentrations (standard solutions) used with spectrophotometers.

**Calomel Electrode.** A reference electrode of known potential consisting of mercury, mercury chloride (calomel), and potassium chloride solution; used to measure pH and electromotive force. Also known as calomel half-cell; calomel reference electrode.

**Calomel Half-cell.** See calomel electrode.

**Calomel Reference Electrode.** See calomel electrode.

**Calorimetric Titration.** See thermometric titration.

**Candoluminescence Spectrophotometry.** Analytical technique based on the luminescence which occurs when inert inorganic matrices (e.g.,  $\text{CaO}-\text{CaSO}_4$ ;  $\text{Mg}(\text{OH})_2$ ) containing activating ions are placed in the edge of a hydrogen flame in air.

**Capillary Condensation.** Condensation of an absorbed vapour within the pores of the adsorbate.

**Capillary Gas Chromatography.** A highly efficient type of gas chromatography in which the gaseous sample passes through capillary tubes with internal diameters between 0.2 and 0.5 millimeter and lengths up to 100 meters, and absorption takes place on a medium that is spread on the inner walls of these tubes.

**Carbon-12.** A stable isotope of carbon with mass number of 12, forming about 98.9% of natural carbon; used as the basis of the newer scale of atomic masses, having an atomic mass of exactly 12 u (relative nuclidic mass unit) by definition.

**Carbon-14.** A naturally occurring radioisotope of carbon having a mass number of 14 and half-life of 5780 years; used in radio-carbon dating and in the elucidation of the metabolic path of carbon in photosynthesis. Also known as radiocarbon.

**Carbon-hydrogen Analyzer.** A device used in the quantitative analysis of the carbon and hydrogen content of organic compounds.

**Carbon Number.** The number of carbon atoms in a material under analysis; plotted against chromatographic retention volume for compound identification.

**Carbon Residue Test.** A destructive-distillation method for estimation of carbon residues in fuels and lubricating oils. Also known as Conradson carbon test.

**Carbylamine Reaction.** A qualitative test for primary amines carried out by warming the suspected amine with chloroform and an alcoholic solution of potassium hydroxide. Under these conditions primary amines produce the intensely nauseating odour characteristic of the carbylamines (isonitriles). Sometimes used as a test for chloroform, but it is not specific, as bromoform, iodoform and chloral also react in the same manner.

**Carius Method.** A procedure used to analyze organic compounds for sulfur, halogens, and phosphorus that involves heating the sample with fuming acid in a sealed tube.

**Carlsbad Law.** A feldspar twin law in which the twinning axis is the c axis, the operation is rotation of  $180^\circ$ , and the contact surface is parallel to the side pinacoid.

**Carius Method.** The quantitative determination of S and halogens in covalent (organic) compounds by complete oxidation of the

compound with conc. nitric acid and subsequent estimation of precipitated  $\text{AgX}$  or  $\text{BaSO}_4$ .

**Carius Tube.** A thick-walled glass tube originally used in the Carius method but used in any reaction involving volatile materials.

**Carmine.** An aluminium lake of the pigment from cochineal (q.v.). Bright red pieces, easily powdered. Soluble in alkali solutions, borax; insoluble in dilute acids; slightly soluble in hot water.

Grades : Technical.

Uses : Dyes, inks, indicator in chemical analysis colouring food materials, medicines, etc.

**Carnot's Reagent.** A solution of sodium bismuth thiosulfate in alcohol used for determining potassium.

**Carrier Gas.** The gas used to carry the sample in gas chromatography.

**Cascade Mixer-settler.** Series of liquid-holding vessels with stirrers, each connected to an unstirred vessel in which solids or heavy immiscible liquids settle out of suspension; light liquid moves through the mixer-settler units, counterflowing to heavy material, in such a manner that fresh liquid contacts treated heavy material, and spent (used) liquid contacts fresh (untreated) heavy material.

**Cascade Tray.** A fractionating apparatus that consists of a series of parallel troughs arranged in stairstep fashion.

**Cathode Efficiency.** The proportion of current used for completion of a given process at the cathode.

**Cathodic Inhibitor.** A compound, such as calcium bicarbonate or sodium phosphate, which is deposited on a metal surface in a thin film that operates at the cathodes to provide physical protection over the entire surface against corrosive attack in a conducting medium.

**Cathodic Polarization.** Portion of electric cell polarization occurring at the cathode.



**Catholyte.** Electrolyte adjacent to the cathode in an electrolytic cell.

**Cation.** A positively charged atom or group of atoms, or a radical which moves to the negative pole (cathode) during electrolysis.

**Cation Analysis.** Qualitative analysis for cations in aqueous solution.

**Cation Exchange.** A chemical reaction in which hydrated cations of a solid are exchanged, equivalent for equivalent, for cations of like charge in solution.

**Cation Exchange Resin.** A highly polymerized synthetic organic compound consisting of a large, nondiffusible anion and a simple, diffusible cation, which later can be exchanged for a cation in the medium in which the resin is placed.

**Cationic Reagent.** A surface-active agent with active positive ions used for ore beneficiation (flotation via flocculation); an example of a cationic reagent is cetyl trimethyl ammonium bromide.

**Cationic Resin.** An ion exchange material that can exchange cations; such as  $H^+$  and  $Na^+$ , for ions in the surrounding medium. Such resins are used for a wide range of purification and analytical purposes.

They are often produced by adding a sulphonic acid group ( $-SO_3^-H^+$ ) or a carboxylate group ( $-COO^-H^+$ ) to a stable polyphenylethene resin. A typical exchange reaction is :



They have been used to great effect to separate mixtures of cations of similar size having the same charge. Such mixtures can be attached to cationic resins and progressive elution will recover them in order of decreasing ionic radius. Promethium was first isolated using this technique.

**Celestine Blue.** A dye used for staining biological specimens.

**Cell.** A cup, jar, or vessel containing electrolyte solutions and metal electrodes to produce an electric current (conductimetric or potentiometric) or for electrolysis (electrolytic).

**Cell Constant.** The ratio of distance between conductance-titration electrodes to the area of the electrodes, measured from the determined resistance of a solution of known specific conductance.

**Centipoise (cp).** One one-hundredth of a poise. The poise is the metric system unit of viscosity, and has the dimensions of dyne-second per square centimeter or grams per centimeter-second.

**Centistock (cs).** One one-hundredth stock, the kinematic unit of viscosity; it is equal to the viscosity in poises divided by the density of the fluid in grams per cubic centimeter, both measured at the same temperature.

**Centrifugal Extractor.** A device for separating components of a liquid solution, consisting of a series of perforated concentric rings in a cylindrical drum that rotates at 2000–5000 revolutions per minute around a cylindrical shaft; liquids enter and leave through the shaft; they flow radially and concurrently in the rotating drum.

**Centrifugal Molecular Still.** A device used for molecular distillation; material is fed to the center of a hot, rapidly rotating cone housed in a chamber at a high vacuum; centrifugal force spreads the material rapidly over the hot surface, where the evaporable material goes off as a vapor to the condenser.

**Centrifugal Pump.** The most widely used pump in the chemical and process industries. It consists of a rotor with a number of curved vanes rotating inside a flat, cylindrical casing. Liquid enters the centre of the casing along the rotor axis and is swept along the vanes into the volute which is a ring-shaped chamber. Hence kinetic energy is converted to pressure energy. Liquid is discharged tangentially through an outlet in the volute.

Centrifugal pumps may be constructed from corrosion-resistant materials. They will not give a high pressure unless several stages are used.

**Centrifugal Sedimentation.** Removing solids from liquids by causing particles to settle through the liquid radially toward or away from the center of rotation (depending on the solid-liquid relative densities) by use of a centrifuge.

**Centrifugal Settler.** Spinning container that separates solid particles from liquids; centrifugal force causes suspended solids to move toward or away from the center of rotation, thus concentrating them in one area for removal.

**Centrifuge Refining.** The use of centrifuges for liquids processing, such as separation of solids or immiscible droplets from liquid carriers, or for liquid-liquid solvent extraction.

**Centrifuge Tube.** Calibrated, tube-shaped glass container used with laboratory centrifuges for volumetric analysis of separable (solid-liquid or immiscible liquid) samples.

**Centrifuges.** Machines which employ centrifugal force to obtain high rates of sedimentation or filtration in order to separate a solid and a liquid or two immiscible liquids. The mixture to be separated is contained in a cylindrical bowl which is rotated at high speed. If the walls of the bowl are permeable (perforate bowl) the liquid will drain through, if not, two years will be formed.

Perforate bowl centrifuges are used chiefly for the filtration and dewatering of coarse materials such as crystals (filtering centrifugals). The bowl axis is normally vertical, and the bowl may be driven from above or below. Although batchwise operation is widely employed labour requirements are high. For this reason automatic batch and continuous machines have been developed, in which loading and unloading of the machine is either automatic or continuous.

Sedimentation centrifuges are used to separate finely divided solids from liquids. They have to develop higher centrifugal fields than filtering centrifugals and therefore have higher speeds of rotation. The bowl is not perforated and the clear liquid leaves over a circular weir at the end. Many centrifuges of this type are continuous; this is achieved by incorporating a helical screw conveyor inside the bowl which scrapes the solid along the walls to the discharge ports.

Centrifuges for separating liquids require high centrifugal fields or must be so designed that the droplets have only to settle through a small distance. The tubular bowl centrifuge has a long bowl of small diameter and revolves at very high speeds (about 15000 r.p.m.). The disc bowl centrifuge has a bowl containing a vertical array of conical discs set close together, and revolves at rather lower speeds than the previous type. Although the centrifugal field is less, the droplets have only to settle through a distance less than the distance between disc, say 1/32 in. In both types the heavier liquid flows to the outside of the bowl and the light liquid to the inside. Operation is invariably continuous.

**Cetane Number.** The percentage by volume of cetane (cetane number 100) in a blend with  $\alpha$ -methylnaphthalene (cetane number 0); indicates the ability of a fuel to ignite quickly after being injected into the cylinder of an engine.

**Cetane Number Improver.** A chemical which has the effect of increasing a diesel fuel's cetane number; examples are nitrates, nitroalkanes, nitrocarbonates, and proxides.

**Chain Balance.** An analytical balance with one end of a fine gold chain suspended from the beam and the other fastened to a device which moves over a graduated vernier scale.

**Channel.** In percolation filtration, a portion of the clay bed where there is a preponderance of flow.

**Channeling.** In chromatography, furrows or breaks in an ion-exchange bed which permit a solution to run through without having contact with active groups elsewhere in the bed.

**Characteristic Loss Spectroscopy.** A branch of electron spectroscopy in which a solid surface is bombarded with monochromatic electrons, and backscattered particles which have lost an amount of energy equal to the core-level binding energy are detected. Abbreviated CLS.

**Characteristic Radiation.** Radiation originating in an atom following removal of an electron, whose wavelength depends only on the element concerned and the energy levels involved.

**Characteristic X-rays.** Electromagnetic radiation emitted as a result of arrangements of the electrons in the inner shells of atoms; the spectrum consists of lines whose wavelengths depend only on the element concerned and the energy levels involved.

**Characterization Factor.** A number which expresses the variations in physical properties with change in character of the paraffinic stock; ranges from 12.5 for paraffinic stocks to 10.0 for the highly aromatic stocks. Also known as Watson factor.

$$\text{Characterization factor } K = T_B^{\frac{1}{3}} d$$

where  $T_B$  = 'average' boiling point in degrees Rankine  
and  $d$  = the specific gravity at 60/60°F.

High values for  $K$  indicate a predominantly paraffinic character while low values indicate aromatic character.

**Charcoal Test.** A determination of the natural gasoline content of natural gas by adsorbing the gasoline on activated charcoal and then recovering it by distillation.

**Charge Transfer.** The process in which an ion takes an electron from a neutral atom, with a resultant transfer of charge.

**Charge-Transfer Complexes.** Compounds in which electrons move between molecules.

**Chelate.** A molecular structure in which a heterocyclic ring can be formed by the unshared electrons of neighbouring atoms.

**Chelating Agent.** An organic compound in which atoms form more than one co-ordinate bonds with metals in solution.

**Chelating Resin.** Any of the ion-exchange resins with unusually high selectivity for specific cations; for example, phenol-formaldehyde resin with 8-quinolinol replacing part of the phenol, particularly selective for copper, nickel, cobalt, and iron(III).

**Chelation.** A chemical process involving formation of a heterocyclic ring compound which contains at least one metal cation or hydrogen ion in the ring.

**Chelometry.** Analytical technique involving the formation of 1 : 1 soluble chelates when a metal ion is titrated with aminopolycarboxylate and polyamine reagents; a form of compleximetric titration.

## Chemical

1. Related to the science of chemistry.
2. A substance characterized by definite molecular composition.

**Chemical Crystallography.** The geometric description, and study, of the internal arrangement of atoms in crystals formed from chemical compounds.

**Chemical Dating.** The determination of the relative or absolute age of minerals and of ancient objects and materials by measurement of their chemical compositions.

**Chemical Dating.** Estimation of the age of geologic structures and events by measuring the amount of radioactive decay products in existing samples. The age of a uranium-containing material can be determined by measuring the percentage of lead (or helium) formed as a result of disintegration of the uranium. Uranium decays to both helium and the 206 lead isotope, but

measurement of helium content is inaccurate because of its strong tendency to escape. By determining the ratio of the percentage of lead in a sample to the percentage of uranium, the age can be calculated. A more recent method, applicable to events within about 10,000 years, involves the use of the natural radioactive carbon isotope (C-14); the percentage of this isotope determined in a carefully prepared sample is an index of its age, based on the half-life of C-14 (5700 years), which was present in the atmospheric  $\text{CO}_2$  absorbed by plants centuries ago. This method has yielded valuable results in the study of archaeological specimens, deep-sea sedimentation and dates of volcanic and glacier activity.

**Chemical-ion Pump.** A vacuum pump whose pumping action is based on evaporation of a metal whose vapour then reacts with the chemically active molecules in the gas to be evacuated.

**Chemical Microscopy.** Application of the microscope to the solution of chemical problems.

**Chemical Polarity.** Tendency of a molecule, or compound, to be attracted or repelled by electrical charges because of an asymmetrical arrangement of atoms around the nucleus.

**Chemical Potential.** In a thermodynamic system of several constituents, the rate of change of the Gibbs function of the system with respect to the change in the number of moles of a particular constituent.

**Chemical Reactor.** Vessel, tube, pipe, or other container within which a chemical reaction is made to take place; may be batch or continuous, open or packed, and can use thermal, catalytic, or irradiation actuation.

**Chemiluminescence.** Emission of light as a result of a chemical reaction without an apparent change in temperature.

**Chemiosmosis.** A chemical reaction occurring through an intervening semi-permeable membrane. Also known as chemosmosis.

**Chemisorption.** A chemical adsorption process in which weak chemical bonds are formed between gas or liquid molecules and a solid surface.

**Chemometrics.** Application of computer data-analysis techniques to the classification, assimilation, and interpretation of chemical information. Its major purpose is to correlate data in such a way that trends or patterns are indicated. Molecular spectra, thermodynamic functions, and distribution of chemicals in the atmosphere in relation to rainfall are some fields to which this science has been utilized. Formal programs in chemometrics are under way at the University of Washington and at Umea University in Sweden.

**Chloramine T**  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NClNa} \cdot 3\text{H}_2\text{O}$ . A white, crystalline powder that decomposes slowly in air, freeing chlorine; used as an antiseptic, a germicide, and an oxidizing agent and chlorinating agent.

**Chlorophenol Red, Dichlorophenolsulphonphthalein.** A sulphonphthalein indicator used in 0.04% aqueous solution. pH range 4.8 (yellow)-6.4 (red).

**Chlorosulfonic Acid**  $\text{ClSO}_3\text{OH}$ . A fuming liquid that decomposes in water to sulfuric acid and hydrochloric acid; used in pharmaceuticals, pesticides, and dyes, and as a chemical intermediate. Also known as chlorosulfuric acid; sulfuric chlorohydrin.

**Christiansen Effect.** Monochromatic transparency effect when finely powdered substances, such as glass or quartz, are immersed in a liquid having the same refractive index.

**Christmas Factor.** A soluble protein blood factor involved in blood coagulation. Also known as factor IX; plasma thromboplastin component (PTC).

**Chromatogram.** A record obtained by chromatography. The term is applied to the developed records of paper chromatography and thin-layer chromatography and also to the graphical record produced in gas chromatography.



**Chromatograph.** To employ chromatography to separate substances.

**Chromatographic Adsorption.** Preferential adsorption of chemical compounds (gases or liquids) in an ascending molecular-weight sequence onto a solid adsorbent material, such as activated carbon, alumina, or silica gel; used for analysis and separation of chemical mixtures.

**Chromatography, Chromatographic Analysis.** A series of closely related techniques of separation of components of a mixture because of the distribution of the components between a liquid phase and a solid phase (stationary phase often silica or alumina) which usually has a large surface area. If the stationary phase is in a tube the technique is column chromatography, when paper or thin layers of stationary phase are used the technique is a sheet technique. The active solid stationary phase is the absorbent, an inert support is the support. The whole process of separation of the sample components into separate bands or zones is the development of the chromatogram and is carried out by elution-the mobile phase being the eluting agent. The whole process gives a chromatogram.

The chromatogram can finally be used as the series of bands or zones of components or the components can be eluted successively and then detected by various means (e.g. thermal conductivity, flame ionization, electron capture detectors or the bands can be examined chemically). If the detection is non-destructive, preparative scale chromatography can separate measurable and useful quantities of components. The final detection stage can be coupled to a mass spectrometer (G.C.M.S.) and to a computer for final identification.

Among the various chromatographic methods are adsorption column chromatography (use of a liquid phase in a solid column of adsorbent), partition column chromatography (distribution between two liquids in a column), thin-layer chromatography (partition on an open thin sheet), paper chromatography

(use of a paper sheet as stationary phase), high pressure liquid chromatography (partition column chromatography under high pressure), ion exchange chromatography (ion exchange), gas chromatography (distribution of a gaseous solute between a gas and a liquid or solid phase), zone electrophoresis (sheet chromatography in the presence of an electric field).

Gel permeation chromatography, exclusion chromatography, gel filtration chromatography. A technique for separating the components of a mixture according to molecular volume differences. A porous solid phase (a polymer, molecular sieve) is used which can physically entrap small molecules in the pores whilst large molecules pass down the column more rapidly. A solvent pressure up to 1000 psi may be used.

**Chronoamperometry.** Electroanalysis by measuring at a working electrode the rate of change of current versus time during a titration; the potential is controlled.

**Chronopotentiometry.** Electroanalysis based on the measurement at a working electrode of the rate of change in potential versus time; the current is controlled.

**Chu.** Abbreviation for centigrade heat unit. It is the amount of heat required to raise the temperature of one pound of water one centigrade degree from 15°C to 16°C. It is sometimes called a pcu (pound centigrade unit).

**Circular Chromatography.** See radial chromatography.

**Circular Paper Chromatography.** A paper chromatographic technique in which migration from a spot in the sheet takes place in 360° so that zones separate as a series of concentric rings.

**Circulating Pump.** Pump used to circulate process liquid out of and back into a process system, as in the circulation of distillation column bottoms through an external heater, or the circulation of storage tank bottoms to mix tank contents.

**Circulating System.** Fluid system in which the process fluid is taken from and pumped back into the system, as in the circulation of distillation column bottoms through an external heater.

**Classification.** The process of separating a mixture of particles into two or more fractions according to size, shape, density, magnetic properties, etc. The material to be classified may consist of a single material to be separated into different size fractions, e.g. by sieving. Alternatively classification may involve separation of a mixture into its constituents as in the removal of dirt from coal.

**Clarification.** The removal from a liquid of small amounts of suspended matter with the object of obtaining a clear product. Clarification may be achieved by filtration, centrifugation, or by the use of a clarifier.

**Clausius-dickel Column.** See thermogravitational column.

**Clinical Chemistry.** A subdivision of chemistry that deals with the behaviour and composition of all types of body fluids, including the blood, urine, perspiration, glandular secretions, etc. It involves analysis and testing of these for content of numerous metabolic constituents, as well as foreign materials; thus it also includes toxicological factors.

**Close-packed Crystal.** A crystal structure in which the lattice points are centers of spheres of equal radius arranged so that the volume of the interstices between the spheres is minimal.

**Cloud Point.** The temperature at which paraffin wax or other solid substance begins to separate from a solution of petroleum oil; a cloudy appearance is seen in the oil at this point.

**Cloudy Crystal-ball Model.** An optical analogy used in explaining scattering of nucleons by nuclei, in which the nucleus is thought of as a sphere of nuclear matter which partially refracts and partially absorbs the incident nucleon (de Broglie) wave. Also known as optical model.

**Coacervation.** The separation, by addition of a third component, of an aqueous solution of a macromolecule colloid (polymer) into two liquid phases, one of which is colloid-rich (the coacervate) and the other an aqueous solution of the coacervating agent (the equilibrium liquid).

**Coal Tar Dye.** Dye made from a coal tar hydrocarbon or a derivative such as benzene, toluene, xylene, naphthalene, or aniline.

**Cobalt-60.** A radioisotope of cobalt, symbol  $^{60}\text{Co}$ , having a mass number of 60; emits gamma rays and has many medical and industrial uses; the most commonly used isotope for encapsulated radiation sources.

**Cold Test.** A test for aviation fuel or similar distillate fuel in which the dried sample is cooled under standard conditions to just below the specified temperature and examined for the presence of crystals.

**Colon.** Any of the small ions entering a solid ion exchanger and having the same charge as that of the fixed ions.

**Coke Number.** A number used to report the results of the Ramsbottom carbon residue test.

**Coke Oven.** A retort in which coal is converted to coke by carbonization.

**Colburn Method.** Graphical method, and equations to calculate the theoretical number of plates (trays) needed to separate light and heavy liquids in a distillation column.

**Colour Indicators.** Indicators (acid base, oxidation-reduction) which depend for their effect on colour change. Screened indicators have an additional dye added which acts as a colour filter and makes the colour change more visible. Thus the colour change of methyl orange with pH is made more obvious by addition of some methylene blue. A universal indicator is a mixture of indicators which shows a gradual but well marked series of

colour changes over a very wide range of pH. Thus a mixture of suitable proportions of methyl orange, methyl red, bromothymol blue, naphthophthalen, phenolphthalein and cresolphthalein changes from red to blue through the colours of the spectrum over the pH range 3.0- 11.5.

**Cold-spot Hygrometer.** See dew-point hygrometer.

**Cold Test.** A test to determine the temperature at which clouding or coagulation is first visible in a sample of oil, as the temperature of the sample is reduced.

**Collateral Series.** A radioactive decay series, initiated by transmutation, that eventually joins into one of the four radioactive decay series encountered in natural radioactivity.

**Collision Broadening.** See collision line-broadening.

**Collision Excitation.** The excitation of a gas by collisions of moving charged particles.

**Collision Ionization.** The ionization of atoms or molecules of a gas or vapour by collision with other particles.

**Collision Line-broadening.** Spreading of a spectral line due to interruption of the radiation process when the radiator collides with another particle. Also known as collision broadening.

**Colorimetric Analysis.** Quantitative analysis of solutions by estimating their colour, e.g., by comparing it with the colours of standard solutions.

**Color Comparator.** A photoelectric instrument that compares an unknown color with that of a standard color sample for matching purposes. Also known as photoelectric color comparator.

**Colorimeter.** A device for measuring concentration of a known constituent in solution by comparison with colors of a few solutions of known concentration of that constituent. Also known as chromometer.

**Color Standard.** Liquid solution of known chemical composition and concentration, hence of known and standardized color, used for optical analysis of samples of unknown strength.

**Color Test.** The quantitative analysis of a substance by comparing the intensity of the color produced in a sample by a reagent with a standard color produced similarly in a solution of known strength.

**Color Throw.** In an ion-exchange process, discoloration of the liquid passing through the bed.

**Column.** See tower.

**Column Bleed.** The loss of carrier liquid during gas chromatography due to evaporation into the gas under analysis.

**Column Chromatography.** Chromatographic technique of two general types; packed columns usually contain either a granular adsorbent or a granular support material coated with a thin layer of high-boiling solvent (partitioning liquid); open-tubular columns contain a thin film of partitioning liquid on the column walls and have an opening so that gas can pass through the center of the column.

**Column Development Chromatography.** Columnar apparatus for separating or concentrating one or more components from a physical mixture by use of adsorbent packing; as the specimen percolates along the length of the adsorbent, its various components are preferentially held at different rates, effecting a separation.

Column chromatography employs a solid stationary phase, such as alumina or silica gel, packed in a vertical tube. The sample mixture is poured in at the top and one or more of its components become attached to the solid phase. These adsorbed fractions can be washed off the column and collected by using an appropriate solvent.

Alumina, which has been activated by heating to remove adsorbed gases, is a strongly polar substance and the ease with which fractions can be removed from the column will depend on the polarity of their molecules. Careful choice of the solvent (eluent) used for the washing will allow the fractions to be selectively removed from the column. A non-polar solvent is used initially and is gradually replaced by a more polar solvent.

Compare thin-layer chromatography.

**Combination Principle.** See Ritz's combination principle.

**Combination Unit.** A processing unit that combines more than one process, such as straight-run distillation together with selective cracking.

**Combination Vibration.** A vibration of a polyatomic molecule involving the simultaneous excitation of two or more normal vibrations.

**Combined Carbon.** Carbon that is chemically combined within a compound, as contrasted with free or uncombined elemental carbon.

**Combined Cyanide.** The cyanide portion of a complex ion composed of cyanide and a metal.

**Combining Weight.** The weight of an element that chemically combines with 8 grams of oxygen or its equivalent.

**Combustion.** The burning of gas, liquid, or solid, in which the fuel is oxidized, evolving heat and often light.

**Combustion Efficiency.** The ratio of heat actually developed in a combustion process to the heat that would be released if the combination were perfect.

**Combustion Furnace.** A heating device used in the analysis of organic compounds for elements

**Combustion Rate.** The rate of burning of any substance.

**Combustion Train.** The arrangement of apparatus for elementary organic analysis.

**Combustion Tube.** A glass, silica, or porcelain tube, resistant to high temperatures, that is a component of a combustion train.

**Common-ion Effect.** The lowering of the degree of ionization of a compound, when another ionizable compound is added to a solution; the compound added has a common ion with the other compound.

**Comparator-densitometer.** Device that projects a labeled spectrum onto a screen adjacent to an enlarged image of the spectrum to be analyzed, allowing visual comparison.

**Comparison Spectrum.** A line spectrum whose wavelengths are accurately known, and which is matched with another spectrum to determine the wavelengths of the latter.

**Competing Equilibria Condition.** The competition for a reactant in a complex chemical system in which several reactions are taking place at the same time.

**Complexing Agent.** A substance capable of forming a complex compound with another material in solution.

**Complexometric Analysis.** A type of volumetric analysis in which the reaction involves the formation of an inorganic complex.

**Complex Ion.** A complex, electrically charged group of atoms or radical, for example,  $\text{Cu}(\text{NH}_3)_2^{2+}$ .

**Complexometric Indicator.** See metallochromic indicators.

**Complexometric Titration.** A titration involving formation or decomposition of a complex. Thus  $\text{Fe}^{2+}$  plus  $\text{SCN}^-$  is intense red; titration of the  $\text{Fe}^{3+}$  with EDTA causes decomposition of the red  $\text{Fe}^{3+}$ - $\text{SCN}^-$  complex and formation of the colourless  $\text{Fe}^{3+}$ -EDTA complex.



**Component.**

1. A part of a mixture.
2. The smallest number of chemical substances which are able to form all the constituents of a system in whatever proportion they may be present.

**Component Distillation.** A distillation process in which a fraction that cannot normally be separated by distillation is removed by forming an azeotropic mixture.

**Component Substances Law.** The law that each substance, singly or in mixture, composing a material exhibits specific properties that are independent of the other substances in that material.

**Composition.** The elements or compounds making up a material or produced from it by analysis.

**Composition Diagram.** Graphical plots to show the solvent-solute concentration relationships during various stages of extraction operations (leaching, or solid-liquid extraction; and liquid-liquid extraction).

**Compound Elastic Scattering.** Scattering in which the final state is the same as the initial state, but there is an intermediate state with the colliding systems amalgamating to form a compound system.

**Compound Nucleus.** An intermediate state in a nuclear reaction in which the incident particle combines with the target nucleus and its energy is shared among all the nucleons of the system.

**Compton Incoherent Scattering.** Scattering of gamma rays by individual nucleons in a nucleus or electrons in an atom when the energy of the gamma rays is large enough so that binding effects may be neglected.

**Compton Rule.** An empirical law stating that the heat of fusion of an element times its atomic weight divided by its melting point in degrees Kelvin equals approximately 2.

**Computational Chemistry.** The use of calculations to predict molecular structure, properties, and reactions.

**Concave Grating.** A reflection grating which both collimates and focuses the light falling upon it, made by spacing straight grooves equally along the chord of a concave spherical or paraboloid mirror surface. Also known as Rowland grating.

**Concentrate.** To increase the amount of a dissolved substance by evaporation.

**Concentrated.** Denoting a solution in which the amount of solute in the solvent is relatively high. The term is always relative; for example, whereas concentrated sulphuric acid may contain 96%  $\text{H}_2\text{SO}_4$ , concentrated potassium chlorate may contain as little as 10%  $\text{KClO}_3$ . Compare dilute.

**Concentration.** The amount of a given substance in a stated unit of a mixture, solution, or ore. Common methods of stating concentration are per cent by weight or by volume; normality; or weight per unit volume, as grams per cubic centimeter or pounds per gallon. The concentration of an atom, ion or molecule in a solution may be indicated by square brackets as  $[\text{Cl}^-]$ . For radioactivity, the concentration is usually expressed as millicuries per milliliter (mc/ml), or millicuries per millimole (mc/mM).

### Concentration Cell

1. Electrochemical cell for potentiometric measurement of ionic concentrations where the electrode potential electromotive force produced is determined as the difference in emf between a known cell (concentration) and the unknown cell.

2. An electrolytic cell in which the electromotive force is due to a difference in electrolyte concentrations at the anode and the cathode.

**Concentration Gradient.** The graded difference in the concentration of a solute throughout the solvent phase.

**Concentration Polarization.** That part of the polarization of an electrolytic cell resulting from changes in the electrolyte concentration due to the passage of current through the solution.

**Concentration Potential.** Tendency for a univalent electrolyte to concentrate in a specific region of a solution.

**Concentration Scale.** Any of several numerical systems defining the quantitative relation of the components of a mixture; for solutions, concentration is expressed as the mass, volume, or number of moles of solute present in proportion to the amount of solvent or total solution.

**Concentric Tube Column.** A carefully insulated distillation apparatus which is capable of very high separating power, and in which the outer vapour-rising annulus of the column is concentric around an inner, bottom-discharging reflux return.

**Condensable Vapors.** Gases or vapours which when subjected to appropriately altered conditions of temperature or pressure become liquids.

**Concentrated.** Denoting a solution in which the amount of solute in the solvent is relatively high. The term is always relative; for example, whereas concentrated sulphuric acid may contain 96%  $\text{H}_2\text{SO}_4$ , concentrated potassium chlorate may contain as little as 100%  $\text{KClO}_3$ . Compare dilute.

**Condensation Temperature.** In boiling-point determination, the temperature established on the bulb of a thermometer on which a thin moving film of liquid coexists with vapour from which

the liquid has condensed, the vapour phase being replenished at the moment of measurement from a boiling-liquid phase.

**Condensed System.** A chemical system in which the vapor pressure is negligible or in which the pressure maintained on the system is greater than the vapour pressure of any portion.

**Condenser.** A device used to cool a vapour to cause it to condense to a liquid.

**Conductimetry.** The scientific study of conductance measurement of solutions; to avoid electrolytic complications, conductance measurements are usually taken with alternating current.

**Conductivity.** The property of a substance mixture that describes its ability to transfer heat or electricity. It is the reverse of resistivity.

**Conductometric Titration.** A titration in which electrical conductance of solution is measured during the course of the titration.

**Configuration.** The three-dimensional spatial arrangement of atoms in a stable or isolable molecule.

**Confining Liquid.** A liquid seal (most often mercury or sodium sulfate brine) that is displaced during the no-loss transfer of a gas sample from one container to another.

**Congeaing Point.** The congealing point of petroleum wax \*or petrolatum\* is the temperature at which molten wax ceases to flow when cooled under standard conditions. A thermometer bulb is covered with molten wax and placed in a bottle. The thermometer is rotated and the congealing temperature is taken as the point at which the wax rotates with the thermometer.

**Congo Red.**  $C_{22}H_{22}N_6Na_2O_6S_2$  An azo dye, sodium diphenyldiazobis- $\alpha$ -naphthylamine sulfonate, used as a biological stain and as an acid-base indicator; it is red in alkaline solution and blue in acid solution.

**Conradson Carbon Test.** See carbon residue test.

**Constant-current Electrolysis.** Electrolysis in which a constant current flows through the cell; used in electrodeposition analysis.

**Constant-Potential Electrolysis.** Electrolysis in which a constant voltage is applied to the cell; used in electrodeposition analysis.

**Contact Adsorption.** Process for removal of minor constituents from fluids by stirring in direct contact with powdered or granulated adsorbents, or by passing the fluid through fixed-position adsorbent (achieved carbon or ion-exchange resin); used to decolorize petroleum lubricating oils and to remove solvent vapours from air.

**Contact Filtration.** A process in which finely divided adsorbent clay is mixed with oil to remove colour bodies and to improve the oil's stability.

**Contemporary Carbon.** The isotopic carbon content of living matter, based on assumption of a natural proportion of carbon-14.

**Contaminant.** Any substance accidentally or unwillingly introduced into air, water, or food products which has the effect of rendering them toxic or otherwise harmful. Examples are sulfur dioxide resulting from combustion of high-sulfur fuels; pesticide residues in vegetables, fish, or other food products; industrial dusts; and radioactive materials resulting from nuclear explosions.

**Continuous Spectrum.** A radiation spectrum which is continuously distributed over a frequency region without being broken up into lines or bands.

**Control Agent.** In process automatic-control work, material or energy within a process system of which the manipulated (controlled) variable is a condition or characteristic.

**Conversion Coefficient.** Also known as conversion fraction; internal conversion coefficient.

1. The ratio of the number of conversion electrons emitted per unit time to the number of photons emitted per unit time in the de-excitation of a nucleus between two given states.
2. In older literature, the ratio of the number of conversion electrons emitted per unit time to the number of conversion electrons plus the number of photons emitted per unit time in the de-excitation of a nucleus between two given states.

**Conversion Electron.** An electron which receives energy directly from a nucleus in an internal conversion process and is thereby expelled from the atom.

**Cool Flame.** A faint, luminous phenomenon observed when, for example, mixture of ether vapour and oxygen is slowly heated; it proceeds by diffusion of reactive molecules which initiate chemicals processes as they go.

**Coprecipitation.** A substance when precipitated from solution may be impure due to the presence of foreign substances adsorbed on the surface of occluded within the bulk of the precipitate particles. The contamination of the precipitate by substances which are normally soluble in the mother liquor is termed coprecipitation.

**Coriolls Operator.** An operator which gives a large contribution to the energy of an axially symmetric molecule arising from the interaction between vibration and rotation when two vibrations have equal or nearly equal frequencies.

**Coriolis Resonance Interactions.** Perturbation of two vibrations of a polyatomic molecule, having nearly equal frequencies, on each other, due to the energy contribution of the Coriolis operator.

**Correlation Index.** An index used to determine the general hydrocarbon type of petroleum fractions. Correlation index

measurement involves the determination of  $d$  (specific gravity at 60/60°F) and  $K$  (average boiling point in Kelvin).

$$Cl = 473.7d - 456.8 + 48640/K$$

Value of  $Cl$  below 15 indicate a predominance of alkanes while a value above 50 indicates a high percentage of aromatics.

**Cotectic Crystallization.** Simultaneous crystallization of two or more solid phases from a single liquid over a finite range of falling temperature without resorption.

**Cottrell Chloridometer.** Used for determination of  $Cl^-$  mercaptans, SH groups by coulometric generation of  $Ag^+$ .

**Cotton Effect.** The characteristics wavelength dependence of the optical rotatory dispersion curve or the circular dichroism curve or both in the vicinity of an absorption band.

**Coude Spectrograph.** A stationary spectrograph that is attached to the tube of a coude telescope.

**Coude Spectroscopy.** The production and investigation of astronomical spectra using a coude spectrograph.

### Coulomb Barrier

1. The Coulomb repulsion which tends to keep positively charged bombarding particles out of the nucleus.
2. Specifically, the Coulomb potential associated with this force.

**Coulomb Excitation.** Inelastic scattering of a positively charged particle by a nucleus and excitation of the nucleus, caused by the interaction of the nucleus with the rapidly changing electric field of the bombarding particle.

**Coulometer.** An electrolytic cell for the precise measurement of electrical quantities or current intensity by quantitative determination of chemical substances produced or consumed.

**Coulometric Analysis.** A technique in which the amount of a substance is determined quantitatively by measuring the total amount of electricity required to deplete a solution of the substance.

**Coulometric Titration.** The slow electrolytic generation of a soluble species which is capable of reacting quantitatively with the substance sought; some independent property must be observed to establish the equivalence point in the reaction.

**Coulometry.** A determination of the amount of an electrolyte released during electrolysis by measuring the number of coulombs used.

**Coulostatic Analysis.** An electrochemical technique involving the application of a very short, large pulse of current to the electrode; the pulse charges the capacitive electrode-solution interface to a new potential, then the circuit is opened, and the return of the working electrode potential value is monitored; the current necessary to discharge the electrode interface comes from the electrolysis of electroactive species in solution; the change in electrode potential versus time results in a plot, the shape of which is proportional to concentration.

**Countercurrent Cascade.** An extraction process involving the introduction of a sample, all at once, into a continuously flowing countercurrent system where both phases are moving in opposite directions and are continuously at equilibrium.

**Countercurrent Distribution.** A profile of a compound's concentration in different ratios of two immiscible liquids.

**Countercurrent Extraction.** A liquid-liquid extraction process in which the solvent and the process stream in contact with each other flow in opposite directions. Also known as countercurrent separation.

**Countercurrent Leaching.** A process utilizing a series of leach tanks and countercurrent flow of solvent through them in reverse order to the flow of solid.



**Cox Chart.** A special semilogarithmic plot of vapour pressure vs. temperature especially useful for the petroleum hydrocarbons. The graph corresponding to each separate hydrocarbon is a straight line. All the lines appear to intersect at a point outside the chart.

**Crackle Test.** A simple test for free water in oil fractions. If no cracking sound is heard when about 10 cm<sup>3</sup> of sample is heated in a dry test tube the water in suspension can be considered to be below about 100 p.p.m.

**Cresolphthalein**  $C_6H_4COOC(C_6H_4(OH)CH_3)_2$ . An acid-base indicator, changes from colourless to red between pH 8.2 and 9.8; reagent.

**Cresol Purple**  $C_6H_4SO_3OC(C_6H_4(OH)CH_3)_2$ . Metacresolsulfonphthalein, an acid-base indicator, showing colour change from red to yellow over the range pH 1.2 to 2.8 and from yellow to purple over the range pH 7.4 to 9.0.

**Cresol Red**  $C_{21}H_{19}O_5S$ . A compound derived from o-cresol and used as an acid-base indicator; colour change is yellow to red pH 0.4 to 1.8, or 7.0 to 8.8, depending on preparation. Also known as ortho-cresolsulfonphthalein.

**Critical Absorption Wavelength.** The wavelength, characteristic of a given electron energy level in an atom of a specified element, at which an absorption discontinuity occurs.

**Critical Condensation Temperature.** The temperature at which the sublimand of a sublimed solid recondenses; used to analyze solid mixtures, analogous to liquid distillation. Also known as true condensing point.

**Critical Constant.** A characteristic temperature, pressure, and specific volume of a gas above which it cannot be liquefied.

**Critical Current Density.** The amount of current per unit area of electrode at which an abrupt change occurs in a variable of an electrolytic process.

**Critical Density.** The density of a substance exhibited at its critical temperature and critical pressure.

**Critical Locus.** The line connecting the critical points of a series of liquid-gas phase-boundary loops, for multicomponent mixtures plotted on a pressure versus temperature graph.

**Critical Micelle Concentration.** The concentration of a micelle (oriented molecular arrangement of an electrically-charged colloidal particle or ion) at which the rate of increase of electrical conductance with increase in concentration levels off or proceeds at a much slower rate.

**Critical Moisture Content.** The average moisture throughout a solid material being dried, its value being related to drying rate, thickness of material, and the factors that influence the movement of moisture within the solid.

### **Critical Point**

1. The temperature and pressure at which two phases of a substance in equilibrium with each other become identical, forming one phase.
2. The temperature and pressure at which two ordinary partially miscible liquids are consolute.

**Critical Potential.** The energy needed to raise an electron to a higher energy level in an atom (resonance potential) or to remove it from the atom (ionization potential).

**Critical Solution Temperature.** The temperature above or below which two liquids are miscible in all proportions. Some pairs of liquids have both an upper and a lower critical solution temperature, that is, they can exist in two phases only in a medium temperature range.

**Crosscurrent Extraction.** Procedure of batchwise liquid-liquid extraction in a separatory funnel; solvent is added to the sample in the funnel, which is then shaken, and the extract phase is allowed to coalesce, then is drawn off.

**Cross Section Per Atom.** The microscopic cross section for a given nuclear reaction referred to the natural element, even though the reaction involves only one of the natural isotopes.

**Crucible.** A dish or other vessel in which substances can be heated to a high temperature.

**Crude Assay.** A procedure for determining the general distillation characteristics and other quality information of crude oil.

**Crude Still.** The distillation equipment in which crude oil is separated in various products.

**Cryogenic Pump.** A vacuum pump in which pressure is reduced by condensing gases on surfaces maintained at about 20 K by means of liquid hydrogen or at 4 K by means of liquid helium. Pressures down to  $10^{-8}$  mm Hg ( $10^{-6}$  Pa) can be maintained, if they are used in conjunction with a diffusion pump, pressures as low as  $10^{-15}$  mm Hg ( $10^{-13}$  Pa) can be reached.

**Cryohydrate.** A salt that contains water of crystallization at low temperatures. Also known as cryosol.

**Cryohydric Point.** The eutectic point of an aqueous salt solution.

**Cryoprecipitate.** The precipitate of a cryoglobulin.

**Cryoscopic Constant.** Equation constant expressed in degrees per mole of pure solvent; used to calculate the freezing-point-depression effects of a soluble.

**Cryoscopy.** A phase-equilibrium technique to determine molecular weight and other properties of a solute by dissolving it in a liquid solvent and then ascertaining the solvent's freezing point.

**Crystal Field Theory.** The theory which assumes that the ligands of a coordination compound are the sources of negative charge which perturb the energy levels of the central metal ion and thus subject the metal ion to an electric field analogous to that within an ionic crystalline lattice.

**Crystal Grating.** A diffraction grating for gamma rays or x-rays which uses the equally spaced lattice planes of a crystal.

**Crystal Growth.** The growth of a crystal, which involves diffusion of the molecules of the crystallizing substance to the surface of the crystal, diffusion of these molecules over the crystal surface to special sites on the surface, incorporation of molecules into the surface at these sites, and diffusion of heat away from the surface.

**Crystal Indices.** See Miller indices.

**Crystal Lattice.** A lattice from which the structure of a crystal may be obtained by associating with every lattice point an assembly of atoms identical in composition, arrangement and orientation.

**Crystallization.** The removal of a solid from solution by increasing its concentration above the saturation point in such a manner that the excess solid separates out in the form of crystals. Successive crystallization or fractional crystallization (the successive removal of the least soluble component) may be used in separation and purification.

**Crystallizers.** Equipment for producing crystals from solutions of crystallizable materials. For materials having large temperature coefficients of solubility a simple tank with an agitator and cooling coils may suffice while, if supersaturation by evaporation is necessary, a slightly modified evaporator may be used. In most cases, however, more specialized equipment is employed.

In vacuum crystallizers a warm, saturated solution is fed to a vessel kept under vacuum. Vapour flashes off and cooling occurs by adiabatic evaporation so that concentration and cooling are effected without the need for heat transfer surfaces. The Wulff-Bock crystallizer is, essentially, an inclined, shallow, open trough, made to rock gently. Cooling occurs by natural convection while the liquid flows from one end to the other. Large crys-

tals are possible but output is low. The double-pipe crystallizer consists of a jacketed pipe with the solution flowing through the pipe and coolant flowing counter-current through the jacket. The inner pipe contains an axial shaft with scraper blades to remove solid from the cooled walls. This crystallizer can deal with viscous liquids; e.g. crystallization of paraffin wax from lubricating oils. Scrapers are also used in the Swenson-Walker crystallizer where hot solution flows along an open, U-shaped trough surrounded by a cooling water jacket and containing a rotating, helical agitator which keeps the crystals in suspension and keeps the cooling surface clean.

The Howard crystallizer consists of cold-jacketed, inverted cone through which solution flows in an upward direction. The crystals formed are kept suspended until they are large enough to fall under gravity to the cone point. This method allows some control of crystal size. The Oslo or Krystal crystallizer is one of the more important continuous, industrial crystallizers. A supersaturated solution is introduced through a central pipe extending to the base of a vertical, cylindrical vessel where a mass of small crystals is kept in suspension by the upward flow of liquid. When the crystals reach an appropriate size they fall to a valve in the base while solution leaves the vessel in a saturated condition. Supersaturation of the inlet liquid is effected by flash evaporation of boiling solution or by addition of hot saturated solution followed by cooling. Oslo crystallizers produce evenly-sized, well-shaped crystals.

**Crystallogram.** A photograph of the x-ray diffraction pattern of a crystal.

**Crystallographic Axis.** One of three lines (sometimes four, in the case of a hexagonal crystal), passing through a common point, that are chosen to have definite relation to the symmetry properties of a crystal, and are used as a reference in describing crystal symmetry and structure.

**Crystallography.** The study of the crystal formation of solids, including x-ray determination of lattice structures, crystal habit, and the shape, form, and defects of crystals. When applied to metals, this science is called metallography (q.v.).

**Crystal Monochromator.** A spectrometer in which a collimated beam of slow neutrons from a reactor is incident on a single crystal of copper, lead, or other element mounted on a divided circle.

**Crystal Symmetry.** The existence of nontrivial operations, consisting of inversions, rotations around an axis, reflections, and combinations of these, which bring a crystal into a position indistinguishable from its original position.

**Crystal System.** One of seven categories (cubic, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic) into which a crystal may be classified according to the shape of the unit cell of its Bravais lattice, or according to the dominant symmetry elements of its crystal class.

**Crystal Violet.** See methyl violet.

**Cupferron (ammonium nitroso-beta-phenylhydroxylamine).**

$C_6H_5N(NO)ONH_4$ . Properties: Creamy-white crystals; m.p. 163—164°C. Soluble in water and alcohol. Derivation: By treating an ethereal solution of beta-phenylhydroxylamine with dry ammonia gas and amyl nitrite.

Uses: Analytical reagent, especially for separation and precipitation of metals, e.g., copper, iron, vanadium.

**Curing Time.** The period of time in which a part is subjected to heat or pressure to cure the resin.

**Current Efficiency.** The ratio of the amount of electricity, in coulombs, theoretically required to yield a given quantity of material in

an electrochemical process, to the amount actually consumed.

**Cyanine Dye  $C_{29}H_{35}N_2I$ .** Green metallic crystals, soluble in water; unstable to light, the dye is used in the photography industry as a chemical sensitizer for film. Also known as iodocyanin; quinoline blue.

**Cyclic Chronopotentiometry.** An analytic electrochemical method in which instantaneous current reversal is imposed at the working electrode, and its potential is monitored with time.

**Cyclic Voltammetry.** An electrochemical technique for studying variable potential at an electrode involving application of a triangular potential sweep allowing one to sweep back through the potential region just covered.

**Cycloidal Mass Spectrometer.** Small mass spectrometer of limited mass range fitted with a special-type analyzer that generates a cycloidal-path beam of the sample mass.

**Czochralski Process.** A method of producing large single crystals by inserting a small seed crystal of germanium, silicon, or other semiconductor material into a crucible filled with similar molten material, then slowly pulling the seed up from the melt while rotating it.

# D

**Dalton.** A unit of mass introduced in comparatively recent years. It designates  $1/16$ th of the mass of oxygen-16, the lightest and most abundant isotope of oxygen. Since this is 15.9949, the dalton is equivalent to 0.9997 mass unit.

**Daniell Cell.** A primary cell with a constant electromotive force of 1.1 volts, having a copper electrode in a copper sulfate solution and a zinc electrode in dilute sulfuric acid or zinc sulfate, the solutions separated by a porous partition or by gravity.

**Dark-line Spectrum.** The absorption spectrum that results when white light passes through a substance, consisting of dark lines against a bright background.

**Dauphine Law.** A twin law in which the twinned parts are related by a rotation of  $180^\circ$  around the *c* axis.

**DDTA.** See derivative differential thermal analysis.

**Dean and Stark Water Content.** A rapid method of determining the water content of solids or liquids (*e.g.* coal, textiles, oil, etc.) with boiling points not less than 575K. The sample is heated under reflux with an organic liquids, such as xylene, immiscible with water. The organic liquid and the water are distilled into a receiver where they separate, the water content being read directly from a graduated tube.

**Deashing.** A form of deionization in which inorganic salts are removed from solution by the adsorption of both the anions and cations by ion-exchange resins.

**Debye-Falkenhagen Effect.** The increase in the conductance of an electrolytic solution when the applied voltage has a very high frequency.



**Debye-Huckel Theory.** A theory of the behaviour of strong electrolytes, according to which each ion is surrounded by an ionic atmosphere of charges of the opposite sign whose behaviour retards the movement of ions when a current is passed through the medium.

**Debye Relaxation Time.** According to the Debye-Huckel theory, the time required for the ionic atmosphere of a charge to reach equilibrium in a current-carrying electrolyte, during which time the motion of the charge is retarded.

**Decantation.** The removal of a liquid from a suspension or from an immiscible heavier liquid by pouring while leaving the latter in the original container.

**Decay Curve.** A graph showing how the activity of a radioactive sample varies with time; alternatively, it may show the amount of radioactive material remaining at any time.

**Decay Gammas.** The characteristic gamma rays emitted during the decay of most radioisotopes.

**Decinormal.** Pertaining to a chemical solution that is one-tenth normality in reference to a 1 normal solution.

**Decoctions.** Pharmaceutical solutions made by boiling a drug with water and filtering.

**Decolorize.** To remove the colour from, as from a liquid.

**Decolorizer.** An agent used to decolorize; the removal of colour may occur by a chemical reaction or a physical reaction.

**Decomposition Point.** In a laboratory distillation the thermometer reading coinciding with the first indications of thermal decomposition of the liquid in the flask.

**Decomposition Potential.** The electrode potential at which the electrolysis current begins to increase appreciably. Also known as decomposition voltage.

**Decomposition Voltage.** See decomposition potential.

**Degree.** Any one of several unit for measuring hardness of water, such as the English or Clark degree, the French degree, and the German degree.

**Degree of Freedom.** Any one of the variables, including pressure, temperature, composition, and specific volume, which must be specified to define the state of a system.

**Degritting.** Removal of fine solid particles (grit) from a liquid carrier by gravity separation (settling) or centrifugation.

**Dehumidification.** The removal of condensable water vapour from a vapour-gas mixture by condensation, absorption or adsorption. The term is most frequently applied to the removal of water vapour from air.

Dehumidification of an air stream may be effected by cooling, either by refrigeration or direct injection of water to provide a large cooling area. All entrained water is removed before the air leaves the dehumidification plant. Where small quantities of dry air are required dehumidification can be carried out using chemical absorbents, e.g. calcium chloride, phosphorus pentoxide, sulphuric acid, etc.

**De La Tour Method.** Measurement of critical temperature, involving sealing the sample in a tube and heating it; the temperature at which the meniscus disappears is the critical temperature.

**Delbruck Scattering.** Elastic scattering of gamma rays by a nucleus caused by virtual electron-positron pair production.

**Demasking.** A process by which a masked substance is made capable of undergoing its usual reactions; can be brought about by a displacement reaction involving addition of, for example, another cation that reacts more strongly with the masking ligand and liberates the masked ion.

**Denitration.** Removal of nitrates or nitrogen. Also known as denitrification.

**Dense Media Separation.** Separation of solids of different density by means of a liquid of intermediate density which allows a 'float and sink' separation. Liquids of suitable density can be obtained by suspending finely-divided solids in water. Magnetite or ferrosilicon used separately or together will produce a gravity range of 1.25-3.4 while a special spheroidal ferro-silicon can extend the range to 3.8. The technique is used for separation of mineral products such as coal, ores or aggregates.

**Density-gradient Column.** A graduated glass tube, filled with a mixture of solutions such that a density gradient is obtained throughout the length of the tube. By using spheres of known density the column can be calibrated and subsequently used for rapid determination of densities of small particles of solid.

**Density Gradient Centrifugation.** Separation of particles according to density by employing a gradient of varying densities; at equilibrium each particle settles in the gradient at a point equal to its density.

**Deoxidation 1.** The condition of a molecule's being deoxidized 2. The process of deoxidizing.

**Deoxidizer.** Any substance which reduces the amount of oxygen in a substance, especially a metal, or reduces oxide compounds. Also known as deoxidant.

**Dephlegmation.** In a distillation operation, the partial condensation of vapour to form a liquid richer in higher boiling constituents than the original vapour.

**Depolarizer.** A substance added to the electrolyte of a primary cell to prevent excessive build-up of hydrogen bubbles by combining chemically with the hydrogen gas as it forms. Also known as battery depolarizer.

**Deposition Potential.** The smallest potential which can produce electrolytic deposition when applied to an electrolytic cell.

**Depth-type Filtration.** Removal of solids by passing the carrier fluid through a mass-filter medium that provides a tortuous path with many entrapments to catch the solids.

**Derichment.** In gravimetric analysis by coprecipitation of salts, a system with  $\lambda$  less than unity, when  $\lambda$  is the logarithmic distribution coefficient expressed by the ratio of the logarithms of the ratios of the initial and final solution concentrations of the two salts.

**Derivative.** A substance that is made from another substance.

**Derivative Differential Thermal Analysis.** A method for precise determination in thermograms of slight temperature changes by taking the first derivative of the differential thermal analysis curve (thermogram) which plots time versus differential temperature as measured by a differential thermocouple. Also known as DDTA.

**Derivative Polarography.** Polarography technique in which the rate of change of current with respect to applied potential is measured as a function of the applied potential ( $di/dE$  vs.  $E$ , where  $i$  is current and  $E$  is applied potential).

**Derivative Thermometric Titration.** The use of a special resistance-capacitance network to record first and second derivatives of a thermometric titration curve (temperature versus weight change upon heating) to produce a sharp endpoint peak.

**Descending Chromatography.** A type of paper chromatography in which the sample-carrying solvent mixture is fed to the top of the developing chamber, being separated as it works downward.

**Desiccant.** A hygroscopic substance such as activated alumina, calcium chloride, silica gel, or zinc chloride. Such substances adsorb water vapour from the air and are used to maintain a dry atmosphere in containers for food packaging, chemical reagents etc.

**Desiccator.** A tightly closed vessel containing a desiccant; used in the laboratory for drying test materials. Some types have partial vacuum.

**Determination.** The finding of the value of a chemical or physical property of a compound, such as reaction-rate determination or specific-gravity determination.

**De Vries Effect.** A relatively short-term oscillation, on the order of 100 years, in the radiocarbon content of the atmosphere, and the resulting variation in the apparent radiocarbon age of samples.

**Dew Point.** Temperature at which air is saturated with moisture, or in general the temperature at which a gas is saturated with respect to a condensable component.

**Dew-point Boundary.** On a phase diagram for a gas-condensate reservoir (pressure versus temperature with constant gas-oil ratios), the area along which the gas-oil ratio approaches zero.

**Dew-point Composition.** The water vapour-air composition at saturation, that is, at the temperature at which water exerts a vapour pressure equal to the partial pressure of water vapour in the air-water mixture.

**Dew-point Curve.** On a PVT phase diagram, the line that separates the two-phase (gas-liquid) region from the one-phase (gas) region, and indicates the point at a given gas temperature or pressure at which the first dew or liquid phase occurs.

**Dew-point Depression.** Reduction of the liquid-vapour dew point of a gas by removal of a portion of the liquid (such as water) from the gas (such as air).

**Dew-point Hygrometer.** An instrument for determining the dew point by measuring the temperature at which vapour being cooled in a silver vessels begins to condense. Also known as cold-spot hygrometer.

**Dew-point Pressure.** The gas pressure at which a system is at its dew point, that is, the conditions of gas temperature and pressure at which the first dew or liquid phase occurs.

**Dextrorotatory.** Having the property when in solution of rotating the plane of polarized light to the right or clockwise. Dex-

trorotatory compounds are given the prefix *d* or (+) to distinguish them from their levorotatory, *l* or (—) isomers. The plus sign (+) is preferred.

**Dextrose Equivalent.** (D.E.). The total amount of reducing sugars expressed as dextrose that is present in a corn syrup, calculated as a percentage of the total dry substance. The usual technique for determining D.E. in the corn products industry is the volumetric alkaline copper method.

**Dialysis.** A process of selective diffusion through a membrane; usually used to separate low-molecular-weight solutes which diffuse through the membrane from the colloidal and high-molecular-weight solutes which do not.

**Dialyzate.** The material that does not diffuse through the membrane during dialysis; alternatively, it may be considered the material that has diffused.

**Dialyzer 1.** The semipermeable membrane used for dialyzing liquid. **2.** The container used in dialysis; it is separated into compartments by membranes.

**Diastereoisomer.** One of a pair of optical isomers which are not mirror images of each other. Also known as diastereomer.

**Diastereotopic Ligand.** A ligand whose replacement or addition gives rise to diastereomers.

**Diazoate.** A salt with molecular formula of the type  $C_6H_5N=NOOM$ , where M is nonvalent metal.

**Diazo Compound.** An organic compound containing the radical  $-N=N-$ .

**Diazonium Salts.** Compounds of the type  $R.X.N : N$ , with X being an acid radical such as chlorine.

**Diazotization.** The reaction of a primary aromatic amine with nitrous acid in the presence of excess mineral acid to produce a diazo ( $-N=N-$ ) compound. Widely used in organic synthesis, especially production of dyes.

**Diazo Process.** See diazotization.

**Dibasic.** 1. Compounds containing two hydrogens that may be replaced by a monovalent metal or radical. 2. An alcohol that has two hydroxyl groups, for example, ethylene glycol.

**Dibasic Acid.** An acid having two hydrogen atoms capable of replacement by two basic atoms or radicals.

**Dication.** A doubly charged cation with the general formula  $X^{2+}$ .

**Dichroic.** A term used in crystallography to denote crystals which refract incident light in two directions, thus displaying two colours when observed from different angles, for example, calcite. See also anisotropic; birefringent.

**Dichromatic.** Characterizing certain dyes and indicators for which different colours may be seen depending on the thickness of the solution viewed.

**Dichromate.** A salt of dichromic acid, usually orange or red.

**Dichromatic Dye.** Dye or indicator in which different colours are seen, depending upon the thickness of the solution.

**Dielectric Constant.** A value that serves as an index of the ability of a substance to resist the transmission of an electrostatic force from one charged body to another, as in a condenser. The lower the value, the greater the resistance. The standard apparatus utilizes a vacuum, whose dielectric constant is 1; in reference to this various materials interposed between the charged terminals have the following values at 20° C; air, 1.00058; glass, 3; benzene, 2.3; acetic acid, 6.2; ammonia, 15.5; ethyl alcohol, 25; glycerol, 56; and water, 81. The exceptionally high value for water accounts for its unique behaviour as a solvent and in electrolytic solutions. Most hydrocarbons have high resistance (low conductivity). Dielectric constant values decrease as the temperature rises.

**Dielectric Strength.** The maximum electric field that an insulator or dielectric can withstand without breakdown, usually measured

in kilovolts per centimeter. At breakdown a considerable current passes as an arc, usually with more or less decomposition of the material along the path of the current.

**Dielectric Vapour Detector.** Apparatus to measure the change in the dielectric constant of gases or gas mixtures; used as a detector in gas chromatographs to sense changes in carrier gas.

**Dielectronic Recombination.** The combination of an electron with a positive-ion in a gas, so that the energy released is taken up by two electrons of the resulting atom.

**Dielectrophoresis.** The ability of an uncharged material to move when subjected to an electric field.

**Diene Value.** A number that represents the amount of conjugated bonds in a fatty acid or fat.

**Diesel Index.** An empirical expression for the correlation between the aniline number of a diesel fuel and its ignitability.

**Differential Chemical Reactor.** A flow reactor operated at constant temperature and very low concentrations (resulting from very short residence times), with product and reactant concentrations essentially constant at the levels in the feed.

**Differential Ebulliometer.** Apparatus for precise and simultaneous measurement of both the boiling temperature of a liquid and the condensation temperature of the vapours of the boiling liquid.

**Differential Extraction.** Theoretical limiting case of crosscurrent extraction in a single vessel where feed is continuously extracted with infinitesimal amounts of fresh solvent; true differential extraction cannot be achieved.

**Differential Gravimetric Analysis (DGA).** A variation of differential thermal analysis in which additional information is obtained by determining the rate of change in weight during the heating process.

**Differential Polarography.** Technique of polarographic analysis which measures the difference in current flowing between two



identical dropping-mercury electrodes at the same potential but in different solutions.

**Differential Process.** A process in which a system is caused to move through a bubble point and as a result to form two phases, the minor phase being removed from further contact with the major phase; thus the system continuously changes in quantity and composition.

**Differential Reaction Rate.** The order of a chemical reaction expressed as a differential equation with respect to time; for example,  $dx/dt=k(a-x)$  for first order,  $dx/dt=k(a-x)(b-x)$  for second order, and so on, where  $k$  is the specific rate constant,  $a$  is the concentration of reactant  $A$ ,  $b$  is the concentration of reactant  $B$ , and  $dx/dt$  is the rate of change in concentration for time  $t$ .

**Differential Separation.** Release of gas (vapour) from liquids by a reduction in pressure that allows the vapour to come out of the solution, so that the vapour can be removed from the system; differs from flash separation, in which the vapour and liquid are kept in contact following pressure reduction.

**Differential Spectrophotometry.** Spectrophotometric analysis of a sample when a solution of the major component of the sample is placed in the reference cell; the recorded spectrum represents the difference between the sample and the reference cell.

**Differential Thermal Analysis. (DTA).** The method of precisely measuring the temperature, and the rate of temperature change as heat is added to or abstracted from a sample of material that is in a controlled constant environment. The method determines whether the sample is a pure substance or a mixture, and yields information about its composition and thermal properties.

**Differential Titration.** Thermometric titration in which titrant is added simultaneously to the reaction mixture and to a blank in identically equipped cells.

**Differential Titration.** Analysis of a sample which contains two or more similarly reacting species which are differentiated e.g. use of different bases or indicators.

**Diffraction Grating.** An optical device consisting of an assembly of narrow slits or grooves which produce a large number of beams that can interfere to produce spectra. Also known as grating.

**Diffraction, Neutron.** An analytical technique analogous to x-ray diffraction in which an incident beam of neutrons is scattered by the atoms of a crystal. Because elements that are close to each other in the Periodic Table differ considerably in their neutron-scattering ability, neutron diffraction is capable of distinguishing between them. For example, carbon, nitrogen, and oxygen atoms can be readily identified by neutron diffraction, whereas they appear almost identical by the x-ray method. More accurate determination of the bond lengths of light atoms and distribution of molecular bonding electrons is also possible. Details of molecular structure that can only be inferred by other techniques can often be observed directly by neutron diffraction: Investigations using this method include hydrogen bonding, so-called metal cluster compounds (C-H-M relationships) and electronic charge distributions.

**Diffraction Spectrum.** Parallel light and dark or coloured bands of light produced by diffraction.

**Diffraction Symmetry.** Any symmetry in a crystal lattice which causes the systematic annihilation of certain beams in x-ray diffraction.

**Diffraction, X-ray.** A method of spectroscopic analysis involving the reflection or scattering of x-radiation by the atoms of a substance (lattice) as the rays pass through it. The rays are reflected by the atoms at an angle that is characteristic of the substance, yielding a spectrum that indicates its atomic or molecular structure. The spectra thus obtained are well-defined and specific; from them the properties of elements, and the structure of both crystalline and amorphous materials

can be obtained. For example, unvulcanized rubber gives an amorphous pattern, while vulcanized rubber is crystalline; the cellulose macromolecule has alternating crystalline and amorphous areas. X-ray diffraction was one of the earliest and most successful methods of instrumental analysis; developed by Bragg and von Laue early in this century, it was used with dramatic effect by Moseley (1912) in establishing the location of several elements in the Periodic System. See also lattice; crystal; x-radiation.

**Diffractionmetry.** The science of determining crystal structures by studying the diffraction of beams of x-rays or other waves.

**Diffuse Series.** A series occurring in the spectra of many atoms having one, two, or three electrons in the outer shell, in which the total orbital angular momentum quantum number changes from 2 to 1.

**Diffuse Spectrum.** Any spectrum having lines which are very broad even when there is no possibility of line broadening by collisions.

**Diffusion Barrier.** Porous barrier through which gaseous mixtures are passed for enrichment of the lighter-molecular-weight constituent of the diffusate; used as a many-stage cascade system for the recovery of  $^{235}\text{UF}_6$  isotopes from a  $^{238}\text{UF}_6$  stream.

**Diffusion Current.** In polarography with a dropping-mercury electrode, the flow that is controlled by the rate of diffusion of the active solution species across the concentration gradient produced by the removal of ions or molecules at the electrode surface.

**Diffusion Flame.** A long gas flame that radiates uniformly over its length and precipitates free carbon uniformly.

**Diffusiophoresis.** A process in a scrubber whereby water vapour moving toward the cold water surface carries particulates with it.

**Diffusion Pump.** A non-mechanical pump used for the production of high vacuum. Gas molecules are forced through a fine jet

by molecular bombardment with a stream of oil or mercury vapour from a boiler. Once through the jet the heavy vapour is condensed and returned to the boiler while the expelled gas is removed by a mechanical backing pump.

**Diffusivity Analysis.** Analysis of difficult-to-separate materials in solution by diffusion effects, using, for example, dialysis, electrodialysis, interferometry, amperometric titration, polarography, or voltammetry.

**Dilatancy.** The property of a viscous suspension which sets solid under the influence of pressure.

**Dilatant.** A material with the ability to increase in volume when its shape is changed.

**Diluent.** An inert substance added to some other substance or solution so that the volume of the latter substance is increased and its concentration per unit volume is decreased.

**Dilute.** To make less concentrated.

**Dilute Solution.** A dilute solution is one which contains only a small amount of solute.

**Dilute Phase.** In liquid-liquid extraction, the liquid phase that is dilute with respect to the material being extracted.

**Dilution.** Increasing the proportion of solvent to solute in any solution and thereby decreasing the concentration of the solute per unit volume.

**Dilution, Infinite.** With electrolyte solutions the equivalent conductivity ( $A$ ) increases as the solution is diluted. If  $A$  is extrapolated to zero concentration, the limiting value,  $A_0$ , is called the equivalent conductivity at infinite dilution.

**Dimorphism.** Having crystallization in two forms with the same chemical composition.

**Diphenylamine.** (DPA; N-phenylaniline)  $(C_6H_5)_2NH$ . Properties : Colourless to grayish crystals. Soluble in carbon disulfide, benzene, alcohol, and ether; insoluble in water. Sp. gr. 1.159 :

m.p. 52.85°C; b.p. 302°C; flash point 307°F (152.7°C); autoignition temp. 1173°F (633°C); combustible.

**Derivation :** By heating equal formula weights of aniline and aniline hydrochloride in an autoclave. The product is boiled with dilute hydrochloric acid to remove the unaltered aniline, and the residue is distilled.

**Grades :** Technical; refined, flake and fused.

**Containers :** 50-lb polyethylene-lined paper bags; fibre drums.

**Hazard :** Toxic by ingestion. Tolerance, 10 mg per cubic meter of air.

**Uses :** Rubber antioxidants and accelerators; solid rocket propellants; pesticides; dyes pharmaceuticals; veterinary medicine; storage preservation of apples; stabilizer for nitrocellulose; analytical chemistry.

**Diphenylcarbazine.**  $\text{CO}(\text{NHNHC}_6\text{H}_5)_2$ . White powder, melting point 170°C; used as an indicator, pink for alkalies, colourless for acids.

**Diphenylbenzidine.**  $\text{C}_6\text{H}_5\text{HNC}_6\text{H}_4\text{C}_6\text{H}_4\text{NHC}_6\text{H}_5$ .

**Properties :** White powder. Insoluble in water; slightly soluble in alcohol and acetone; soluble in boiling toluene. Sensitive to light. M.p. 242°C.

**Derivation :** Diphenylamine and fuming sulfuric acid.

**Containers :** Glass bottles.

**Hazard :** May be carcinogenic.

**Use :** Determination of zinc and nitrites.

**Diploid.** A crystal form in the isometric system having 24 similar quadrilateral faces arranged in pairs.

**Dipolar Ion.** An ion carrying both a positive and a negative charge. Also known as zwitterion.

**Dipole.** An assemblage of atoms or subatomic particles having equal electric charges of opposite sign separated by a finite

distance; for instance the proton and orbital electron of a hydrogen atom, or the hydrogen and chlorine atoms of an HCl molecule.

**Dipole Moment.** Molecules in which the atoms and their electrons and nuclei are so arranged that one part of the molecule has a positive electrical charge while the other part is negatively charged. The molecule therefore becomes a small magnet or dipole. Changing electrical or magnetic fields causes the molecule to turn or rotate in one direction or another, depending on the charges of the field. The dipole moment ( $\mu$ ) is the distance between the charges multiplied by the quantity of charge in electrostatic units.

**Dipole Transition.** A transition of an atom or nucleus from one energy state to another in which dipole radiation is emitted or absorbed.

**Direct Effect.** A chemical effect caused by the direct transfer of energy from ionizing radiation to an atom or molecule in a medium.

**Direct-fired Evaporator.** An evaporator in which the flame and combustion gases are separated from the liquid boiling by a metal wall, or other heating surface.

**Direct Nuclear Reaction.** A nuclear reaction which is completed in the time required for the incident particle to transverse the target nucleus, so that it does not combine with the nucleus as a whole but interacts only with the surface or with some individual constituent.

**Direct-vision Spectroscope.** A spectroscope that allows the observer to look in the direction of the light source by means of an Amici prism.

**Disc. (Disk).** A small, thin, circular section or platelet of a material, especially of a biological specimen. "Disc" is the spelling preferred by scientists.

**Discharge Liquor.** Liquid that has passed through a processing operation. Also known as effluent; product.

**Discrete Spectrum.** A spectrum in which the component wavelengths constitute a discrete sequence of values rather than a continuum of values.

**Disk-and-doughnut.** A type of fractionating tower construction of alternating disks and plates that are doughnut-shaped, to provide mixing.

**Disk Colorimetre.** A device for comparing standard and sample colours by means of rotating colour disks.

**Disorder.** Departures from regularity in the occupation of lattice sites in a crystal containing more than one element.

**Dispersion Force.** The force of attraction that exists between molecules that have no permanent dipole.

**Dispersion Relation.** A relation between the cross section for a given effect and the de Broglie wavelength of the incident particle, which is similar to a classical dispersion formula.

**Displacement.** A chemical reaction in which an atom, radical, or molecule displaces and sets free an element of a compound.

**Displacement Chromatography.** Variation of column-development or elution chromatography in which the solvent is sorbed more strongly than the sample components; the freed sample migrates down the column, pushed by the solvent.

**Dissociation Energy.** The energy required for complete separation of the atoms of a molecule.

**Dissociation Pressure.** The pressure, for a given temperature, at which a chemical compound dissociates.

**Dissociative Recombination.** The combination of an electron with a positive molecular ion in a gas followed by dissociation of the molecule in which the resulting atoms carry off the excess energy.

**Dissolved air Flotation.** A liquid-solid separation process wherein the main mechanism of suspended-solids removal is the change

of apparent specific gravity of those suspended solids in relation to that of the suspending liquid by the attachment of small gas bubbles formed by the release of dissolved gas to the solids.

**Dissolved Oxygen (D.O.).** One of the most important indicators of the condition of a water supply for biological, chemical and sanitary investigations. Adequate dissolved oxygen is necessary for the life of fish and other aquatic organisms and is an indicator of corrosivity of water, photosynthetic activity, septicity, etc.

**Dissymmetry Coefficient.** Ratio of the intensities of scattered light at  $45^\circ$  and  $135^\circ$ , used to correct for destructive interference encountered in light-scattering—photometric analyses of liquid samples.

**Distillate.** The products of distillation formed by condensing vapours.

**Distillation.** A separation process in which a liquid is converted to vapour and the vapour then condensed to a liquid. The latter is referred to as the distillate, while the liquid material being vaporized is the charge or distilland. Distillation is thus a combination of evaporation, or vaporization, and condensation. Simple examples are the natural cycle of evaporation and condensation of steam from a tea kettle on a cold surface.

The usual purpose of distillation is purification, or separation of the components of a mixture. This is possible because the composition of the vapour is usually different from that of the liquid mixture from which it is obtained. Alcohol has been so purified for generations to separate it from water, fusel oil, and aldehydes produced in the fermentation process. Gasoline, kerosine, fuel oil and lubricating oil are produced from petroleum by distillation. It is the key operation in removing salt from sea water. Distillation is extensively used in chemical analysis, in laboratory research, and for manufacture of many chemical products. See also destructive distillation, batch distillation, extractive distillation, rectification, dephleg-



mation, flash distillation, continuous distillation, simple distillation, reflux, fractional distillation, azeotropic distillation, vacuum distillation, molecular distillation, and hydrodistillation.

**Distillation column.** A still for fractional distillation.

**Distillation Curve.** The graphical plot of temperature versus overhead product (distillate) volume or weight for a distillation operation.

**Distillation Loss.** In a laboratory distillation, the difference between the volume of liquid introduced into the distilling flask and the sum of the residue and condensate received.

**Distillation Range.** The difference between the temperature at the initial boiling point and at the point of a distillation test.

**Distillation Test.** A standardized procedure for finding the initial, intermediate, and final boiling points in the boiling range of petroleum products.

**Distilled Water.** Water that has been freed of dissolved or suspended solids and organisms by distillation.

**Distilling Flask.** A round-bottomed glass flask that is capable of holding a liquid to be distilled.

**Distribution Coefficient.** The ratio of the amounts of solute dissolved in two immiscible liquids at equilibrium.

**Distribution Law.** The law stating that if a substance is dissolved in two immiscible liquids, the ratio of its concentration in each is constant.

**Distribution Octane Number.** A specialized octane rating to allow for the fact that the more volatile constituents of gasoline tend to have a lower octane number than the heavier components. On full throttle the higher-boiling materials may be retained in the inlet manifold producing a transient knocking effect. An engine test method has been devised with a special manifold to hold back some of the heavier fractions.

**Diver Method.** Measure of the size of suspended solid particles; small glass divers of known density sink to the level where the liquid-suspension density is equal to that of the diver, allowing calculation of particle size. Also known as Berg's diver method.

**DL.** A prefix indicating that a compound contains equal parts of D and L stereoisomers. Small capitals are conventionally used to indicate the right and left-handed structure of such molecules; they do not indicate rotation. See also *dl*; racemic; meso-; enantiomer.

**DI.** A prefix denoting a crystal that rotates the plane of polarized light equally to both left and right, resulting in optical inactivity. The symbol  $\pm$  is preferably used.

**D Line.** The yellow line that is the first line of the major series of the sodium spectrum; the doublet in the Fraunhofer lines whose almost equal components have wavelengths of 5895.93 and 5889.96 angstroms respectively.

**Dobbin's Reagent.** A mercuric chloride—potassium iodide reagent used to test for caustic alkalies in soap.

**Dobson Spectrophotometer.** A photoelectric spectrophotometer used in the determination of the ozone content of the atmosphere; compares the solar energy at two wavelengths in the absorption band of ozone by permitting the radiation of each to fall alternately upon a photocell.

**Doctor Roll.** Roller device used to remove accumulated filter cake from rotary filter drums.

**Doctor Solution.** Sodium plumbite solution used to remove mercaptan sulfur from—gasoline and other light petroleum distillates; used in doctor treatment.

**Doctor Test.** A procedure using doctor solution (sodium plumbite) to detect sulfur compounds in light petroleum distillates which react with the sodium plumbite.

**Doctor Treatment.** A method of improving or "sweetening" the odor of gasoline, petroleum solvents, or kerosine. A doctor solution of sodium plumbite,  $\text{Na}_2\text{PbO}_2$ , is made by dissolving litharge in caustic soda solution; the feed to be sweetened is passed through the doctor solution. The action of the sodium plumbite and the lead sulfide formed from it, in conjunction with free sulfur (either naturally present, or added) converts the malodorous mercaptans to the pleasanter disulfides.

**Documentation.** The techniques involved in recording, coding, storing, and retrieving technical data; it is also called information processing and data processing. It can be performed mechanically by means of a punched card system, of which there are many variations; electronically by means of input to a computer; or by a combination of these methods. One of the most sophisticated techniques for storage and retrieval of chemical information has been developed by Chemical Abstracts Service (q.v.), which includes structural formulas. Pioneer development work in documentation was done by Dyson, Perry, Crane, Tate, and others.

**Doppler Broadening.** Frequency spreading that occurs in single-frequency radiation when the radiating atoms, molecules, or nuclei do not all have the same velocity and may each give rise to a different Doppler shift.

**Doppler-free Spectroscopy.** Any of several techniques which make use of the intensity and monochromatic nature of a laser beam to overcome the Doppler broadening of spectral lines and measure their wavelengths with extremely high accuracy.

**Doppler-free Two-photon Spectroscopy.** A version of Doppler free spectroscopy in which the wavelength of a transition induced by the simultaneous absorption of two photons is measured by placing a sample in the path of a laser beam reflected on itself, so that the Doppler shifts of the incident and reflected beams cancel.

**Dorn Effect.** A difference in a potential resulting from the motions of particles through water; the potential exists between the particles and the water.

**Dosimetry (Radiation).** Measurement of the amount of radiation delivered to the body of an individual. The permissible dose is the quantity of radiation which may be received by an individual over a given period with no detectable harmful effects. For x-or gamma ray exposure the permissible dose is 0.3 roentgen per week, measured in air. All working with radioactive materials are expected to wear some device for detecting incident radiation.

**Double-beam Spectrophotometer.** An instrument that uses a photo-electric circuit to measure the difference in absorption when two closely related wavelengths of light are passed through the same medium.

**Double Distribution.** The product distribution resulting from counter double-current extraction, a scheme in which each of the two liquid phases is transferred simultaneously and continuously in opposite directions through an interconnected train of contact vessels.

**Double-hump Fission Barrier.** Two separated maxima in a plot of potential energy against nuclear deformation of an actinide nucleus, which inhibit spontaneous fission of the nucleus and give rise to isomeric states in the valley between the two maxima.

**Double-pipe Exchanger.** Fluid-fluid heat exchanger made of two concentric pipe sections; one fluid (such as a coolant flows in the annular space between pipes, and the other fluid (such as hot process stream) flows through the inner pipe.

**Double Refraction.** Having different refractive indices in different crystallographic directions.

**Doublet.** 1. Two stationary states which have the same orbital and spin angular momentum but which have different total angular momenta, and therefore have slightly different energies due to spin-orbit coupling. 2. Two electrons which are shared between two atoms and give rise to a nonpolar valence bond. 3. Two closely separated spectral lines arising from a transi-

tion between a single state and a pair of states forming a doublet as described in the atomic physics definition.

**Downcomer.** A method of conveying liquid from one tray to the one below in a bubble-tray column.

**Downstream.** Portion of a product stream that has already passed through the system; that portion located after a specific process unit.

**Drag Factor.** Ratio of hindered diffusion rate to unhindered rate through a swollen dialysis membrane. Also known as Faxén drag factor; hindrance factor.

**Draper Effect.** The increase in volume at constant pressure at the start of the reaction of hydrogen and chlorine to form hydrogen chloride; the volume increase is caused by an increase in temperature of the reactants, due to heat released in the reaction.

**Drew Number.** A dimensionless group used in the study of diffusion of a solid material A into a stream of vapour initially composed of substance B, equal to

$$\frac{Z_A (M_A - M_B) + M_B}{(Z_A - Y_{AW})(M_B - M_A)} \cdot \ln \frac{M_V}{M_W}$$

where  $M_A$  and  $M_B$  are the molecular weights of components A and B,  $M_V$  and  $M_W$  are the molecular weights of the mixture in the vapour and at the wall, and  $Y_{AW}$  and  $Z_A$  are the mole fractions of A at the wall and in the diffusing stream, respectively. Symbolized  $N_D$ .

**Drop Point.** The drop point of a grease is the temperature at which a drop of oil or grease falls from an orifice when a small cup of grease is attached to a thermometer and heated. The drop point is below the melting point of a soap in the grease but should not be taken as an indication of the allowable working temperature. Drop point is useful for quality control or specification purposes.

**Dropping-mercury Electrode.** An electrode consisting of a fine-bore capillary tube above which a constant head of mercury is

maintained; the mercury emerges from the tip of the capillary at the rate of a few milligrams per second and forms a spherical drop which falls into the solution at the rate of one every 2-10 seconds.

**Dropping Point.** The temperature at which grease changes from a semisolid to a liquid state under standardized conditions.

**Drum.** Tower or vessel in a refinery into which heated products are conducted so that volatile portions can separate.

**Dry Ashing.** The conversion of an organic compound into ash (decomposition) by a burner or in a muffle furnace.

**Dry Box.** A container or chamber filled with argon, or sometimes dry air or air with no  $\text{CO}_2$ , to provide an inert atmosphere in which manipulation of very reactive chemicals is carried out in the laboratory.

**Dry Cell.** (Leclanche cell). A primary battery having a zinc anode, a carbon or graphite cathode surrounded by manganese dioxide, and a paste containing ammonium chloride as electrolyte. Such batteries are not reversible and therefore have a limited operating life. Their chief use is in flashlights and similar devices requiring low voltage.

**Dry Chemical.** A mixture of inorganic substances containing sodium bicarbonate (or frequently potassium bicarbonate) with small percentages of added ingredients to render it free-flowing and water repellent. Used as a fire extinguisher on fires in electric equipment, oils, greases, gasoline, paints and flammable gases.

**Dry Cleaning.** The process of cleaning fabrics using solvents which dissolve dirt at low temperatures but do not swell fibres. The most widely used cleaning fluids are the highly inflammable hydrocarbons and chlorinated hydrocarbons, particularly  $\text{C}_2\text{Cl}_4$ .

**Dry-desiccant Dehydration.** Use of silica gel or other solid absorbent to remove liquids from gases, such as water from air, or liquid hydrocarbons from natural gas.

**Dry Distillation.** Distillation of materials that are dry.

**Drye.** Any of numerous types of equipment used in the chemical industries to remove water from a product during processing. Space does not permit description of even a few of the great variety and multiplicity of choices available. The major types include the following :

belt	fluid-bed	screw
centrifugal	freeze	spray
convection	pan	tubular
conveyor	rotary drum	tunnel
flash	rotory tray	truck tray
	rotary vacuum	vibrating

**Dry Ice.** Carbon dioxide in the solid form, usually made in blocks to be used as a coolant; changes directly to a gas at  $-78.5^{\circ}\text{C}$  as heat is absorbed.

### Drying.

1. An operation in which a liquid, usually water, is removed from a wet solid in equipment termed a dryer.
2. A process of oxidation whereby a liquid such as linseed oil changes into a solid firm.

**Drying Agent.** Soluble or insoluble chemical substance that has such a great affinity for water that it will abstract water from a great many fluid materials; soluble chemicals are calcium chloride and glycerol, and insoluble chemicals are bauxite and silica gell. Also known as desiccant.

**Drying Equipment.** Gases can be dried using equipment such as fixed-bed adsorption or packed absorption columns, while liquids may be dried by distillation, etc.

For solids various equipment and techniques are used.

Rotary driers, used for large-scale, continuous drying of granular solids, consist of long, slowly-rotating, inclined cylinders. Wet material, fed at the upper end emerges dry

at the other, heating being direct, by the countercurrent passage of hot air or combustion gases or indirect, by heating of the outer shell.

Drum drivers are used for production of a dry solid from a solution or slurry feed. Liquid is fed onto a slowly-rotating, steam-heated drum where evaporation occurs leaving a coating of solid adhering to the surface. Vacuum operation is also possible.

Tunnel driers consist of long tunnels through which pass warm air, the material to be dried being slowly carried by trays, trolleys or conveyor belt. These are extensively used for solid objects such as pottery ware.

Tray or shelf driers are chambers containing trays or shelves on which the materials, usually granular solids, are placed.

Warm air is circulated through the chamber for each batchwise operation.

Spray driers are used to obtain solids in dry powder form by evaporation of droplets of solution. Spray driers are normally large, cylindrical vessels into which solution is sprayed, meeting hot air or combustion gases. This gives very rapid drying.

**Dry Point.** The temperature at which the last drop of liquid evaporates from the bottom of the flask.

**Dualayer Distillate Process.** A process for the removal of mercaptan and oxygenated compounds from distillate fuel oils; treatment is with concentrated caustic Dualayer solution and electrical precipitation of the impurities.

**Dualayer Solution.** A concentrated potassium or sodium hydroxide solution containing a solubilizer; used in the Dualayer distillate process.

**Dual-gravity Valve.** A float-operated valve that operates on the interface between two immiscible liquids of different specific gravities.



**Dühring's Rule.** Relates the vapor pressures of similar substances at different temperatures. A straight or nearly straight line results if the temperature at which a liquid exerts a particular pressure is plotted on a graph against the temperature at which some similar reference liquid exerts the same vapor pressure. Water is most frequently used as a reference liquid since its vapor pressure at various temperatures is well known.

**Dukler Theory.** Relationship of velocity and temperature distribution in thin films on vertical walls; used to calculate eddy viscosity and thermal conductivity near the solid boundary.

**Dumas Method.** A procedure for the determination of nitrogen in organic substances by combustion of the substance.

**Dye.** A colored substance which imparts more or less permanent color to other materials. Also known as dyestuff.

**Dyeing.** The application of color-producing agents to material, usually fibrous or film, in order to impart a degree of color permanence demanded by the projected end use.

**Dyeing Assistant.** Material such as sodium sulfate added to a dye bath to control or promote the action of a textile dye.

**Dystetic Mixture.** A mixture of two or more substances that has the highest possible melting point of all mixtures of these substances.

## E

**Ebullating-bed Reactor.** A type of fluidized bed in which catalyst particles are held in suspension by the upward movement of the liquid reactant and gas flow. Also known as slurry-bed reactor.

**Ebulliometer.** The instrument used for ebulliometry. Also known as ebullioscope.

**Ebulliometry.** The precise measurement of the absolute or differential boiling points of solutions.

**Echelette Grating.** A diffraction grating with coarse groove spacing, designed for the infrared region; has grooves with comparatively flat sides, and concentrates most of the radiation by reflection into a small angular coverage.

**Echelle Grating.** A diffraction grating designed for use in high orders and at angles of illumination greater than  $45^\circ$  to obtain high dispersion and resolving power by the use of high orders of interference.

**Echelon Grating.** A diffraction grating which consists of about 20 plane-parallel plates about 1 centimeter thick, cut from one sheet, each plate extending beyond the next by about 1 millimeter, and which has a resolving power on the order of  $10^6$ .

**Edeleanu Process.** A process for removal of compounds of sulfur from petroleum fractions by an extraction procedure utilizing liquid sulfur dioxide, or liquid sulfur dioxide and benzene.

**Edge-bridging Ligand.** A ligand that forms a bridge over one edge of the polyhedron of a metal cluster structure.

**Edge Dislocation.** A dislocation which may be regarded as the result of inserting an extra plane of atoms, terminating along the line of the dislocation. Also known as Taylor-Orowan dislocation.

**Edman Degradation Technique.** In protein analysis, an approach to amino-end-group determination involving the use of a reagent, phenylisothiocyanate, that can be applied to the liberation of a derivative of the amino-terminal residue without hydrolysis of the remainder of the peptide chain.

**Effect.** An evaporation-condensation unit.

**Edetate.** See ethylenediaminetetraacetic acid (note).

**EDTA** Abbreviation for ethylenediaminetetra-acetic acid.

**EDTAN.** Abbreviation for ethylenediaminetetraacetonitrile.

**EDTA·Na<sub>4</sub>.** Abbreviation for ethylenediaminetetra-acetic acid.

**Effective Area.** Absolute or cross-sectional area of process media involved in the process, such as the actual area of filter media through which a fluid passes, or the available surface area of absorbent contacted by a gas or liquid.

**Effective Molecular Diameter.** The general extent of the electron cloud surrounding a gas molecule as calculated in any of several ways.

**Effective Permeability.** The observed permeability exhibited by a porous medium to one fluid phase when there is physical interaction between this phase and other fluid phases present.

**Effervescence.** The bubbling of a solution of an element or chemical compound as the result of the emission of gas without the application of heat; for example, the escape of carbon dioxide from carbonated water.

**Efficiency.** In an ion-exchange system, a measurement of the effectiveness of a system expressed as the amount of regenerant required to remove a given unit of adsorbed material.

**Efflorescence.** Loss of combined water molecules by a hydrate when exposed to air, resulting in partial decomposition indicated by presence of a powdery coating on the material. This commonly occurs with washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) which loses almost all its water constituent spontaneously.

**Effluent.** Any gas or liquid emerging from a pipe or similar outlet; usually refers to waste products from chemical or industrial plants as stack gases or liquid mixtures.

**Ehrlich's Reagent.**  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{CHO}$  Granular or leafletlike crystals that are soluble in many organic solvents; melting point is  $74^\circ\text{C}$ ; used in the preparation of dyes, as a reagent for arsphe-  
namine, anthranilic acid, antipyrine, indole, and skatole, and as a differentiating agent between true scarlet fever and serum eruptions. Also known as para-dimethylaminobenzaldehyde; 4-dimethylaminobenzenecarbonal.

**Einschluss Thermometer.** All-glass, liquid-filled thermometer, tem-

perature range  $-201$  to  $+360^{\circ}\text{C}$ , used for laboratory test work.

**Einstein Photochemical Equivalence Law.** The law that each molecule taking part in a chemical reaction caused by electromagnetic radiation absorbs one photon of the radiation. Also known as Stark-Einstein law.

**Einstein's Absorption Coefficient.** The proportionality constant governing the absorption of electromagnetic radiation by atoms, equal to the number of quanta absorbed per second divided by the product of the energy of radiation per unit volume per unit wave number and the number of atoms in the ground state.

**Einstein Viscosity Equation.** An equation which gives the viscosity of a sol in terms of the volume of dissolved particles divided by the total volume.

**Elaidinization.** The process of changing the geometric *cis* form of an unsaturated fatty acid or a compound related to it into the *trans* form, resulting in an acid that is more resistant to oxidation.

**Electrical Calorimeter.** Device to measure heat evolved (from fusion or vaporization, for example); measured quantities of heat are added electrically to the sample, and the temperature rise is noted.

**Electrical Equivalent.** In conductometric analysis of electrolyte solutions, an outside, calibrated current source as compared to (equivalent to) the current passing through the sample under analysis; for example, a Wheatstone-bridge balanced reading.

**Electric Desalting.** A process to remove impurities such as inorganic salts from crude oil by settling out in an electrostatic field.

**Electric Dipole Transition.** A transition of an atom or nucleus from one energy state to another, in which electric dipole radiation is emitted or absorbed.

- Electric Precipitation.** A process that utilizes an electric field to improve the separation of hydrocarbon reagent dispersions.
- Electric Quadrupole Transition.** A transition of an atom or molecule from one energy state to another in which electric quadrupole radiation is emitted or absorbed.
- Electrobalance.** Analytical microbalance utilizing electromagnetic weighing; the sample weight is balanced by the torque produced by current in a coil in a magnetic field, with torque proportional to the current.
- Electrocatalysis.** Any one of the mechanisms which produce a speeding up of half-cell reactions on electrode surfaces.
- Electrochemical Cell.** A combination of two electrodes arranged so that an overall oxidation-reduction reaction produces an electromotive force; includes dry cells, wet cells, standard cells, fuel cells, solid-electrolyte cells, and reserve cells.
- Electrochemical Effect.** Conversion of chemical to electric energy, as in electrochemical cells; or the reverse process, used to produce elemental aluminium, magnesium, and bromine from compounds of these elements.
- Electrochemical Emf.** Electrical force generated by means of chemical action, in manufactured cells (such as dry batteries) or by natural means (galvanic reaction).
- Electrochemical Equivalent.** The number of grams of an element or group of elements liberated by the passage of one coulomb of electricity (one ampere for one second).
- Electrochemical Potential.** The difference in potential that exists when two dissimilar electrodes are connected through an external conducting circuit and the two electrodes are placed in a conducting solution so that electrochemical reactions occur.
- Electrochemical Process.** 1. A chemical change accompanying the passage of an electric current, especially as used in the preparation of commercially important quantities of certain chemical substances. 2. The reverse change, in which a chemical

reaction is used as the source of energy to produce an electric current, as in a battery.

**Electrochemical Reduction Cell.** The cathode component of an electrochemical cell, at which chemical reduction occurs (while at the anode, chemical oxidation occurs).

**Electrochemical Series.** A series in which the metals and other substances are listed in the order of their chemical reactivity or electrode potentials, the most reactive at the top and the less reactive at the bottom. Also known as electromotive series.

**Electrochemical Techniques.** The experimental methods developed to study the physical and chemical phenomena associated with electron transfer at the interface of an electrode and solution.

**Electrochemistry.** A branch of chemistry dealing with chemical changes accompanying the passage of an electric current; or with the reverse process, in which a chemical reaction is used to produce an electric current.

**Electrochromatography.** Type of chromatography that utilizes application of an electric potential to produce an electric differential. Also known as electropherography.

**Electrodecantation.** A modification of electrodialysis in which a cell is divided into three sections by two membranes and electrodes are placed in the end sections; colloidal matter is concentrated at the sides and bottom of the middle section, and the liquid that floats to the top is drawn off.

**Electrodeposition Analysis.** An electroanalytical technique in which an element is quantitatively deposited on an electrode.

**Electrode.** Either of two substances having different electromotive activity, which enables an electric current to flow in the presence of an electrolyte. Electrodes are sometimes called plates or terminals. Commercial electrodes are made of a number of materials which vary widely in electrical conductivity, *i.e.* lead, lead dioxide, zinc, aluminum, copper,

iron, manganese dioxide, nickel, cadmium, mercury, titanium, and graphite; research electrodes may be calomel (mercurous chloride), platinum, glass, or hydrogen. Electrodes are essential components of both batteries and electrolytic cells; in batteries the negative plate is the anode and the positive plate the cathode, whereas in electrolytic cells the reverse is the case. Electrodes are also used in welding devices.

**Electrode, Glass.** A thin glass membrane which, when immersed in a suitable liquid medium, develops a measurable electrical potential that can be readily related to the activity of ionic species present in the solution. By appropriate manipulation of the glass composition, careful pretreatment of the glass surface, and reproducible experimental conditions, electrodes can be devised which not only yield information about the concentration of ions in solution but also have the ability to discriminate, in terms of a selective response, between a number of different ions of similar chemical characteristics. Because of their ability to give both qualitative and quantitative information about ions in solution, glass electrodes are widely used for purposes of chemical measurement, especially in electrochemical research.

**Electrode, Hydrogen.** A platinum surface coated with platinum black, immersed in a solution and bathed, with a stream of pure hydrogen gas. The potential developed depends on the equilibrium between the hydrogen gas and the hydrogen ions in solution. Used as a standard reference electrode.

**Electrodeposition.** The precipitation of a material at an electrode as the result of the passage of an electric current through a solution or suspension of the material, for example, alkaline-earth carbonates; rubber from latex; paint films on metal. The electrode is in the shape of the desired article.

**Electrodialysis.** A form of dialysis (q.v.) in which an electric current aids the separation of substances that ionize in solution. Seawater can be desalted by this method on a large scale by placing it in the center chamber of a 3-compartment container having two semipermeable membranes and a positive

electrode in one end chamber and a negative electrode in the other; the ions migrate to their respective electrodes under a difference potential, leaving the water salt-free. See also dialysis; desalination; demineralization.

**Electrode Potential.** Also known as electrode voltage. The voltage existing between an electrode and the solution or electrolyte in which it is immersed; usually, electrode potentials are referred to a standard electrode, such as the hydrogen electrode.

**Electrode Voltage.** See electrode potential.

**Electrodialysis.** Dialysis that is conducted with the aid of an electromotive force applied to electrodes adjacent to both sides of the membrane.

**Electrodialyzer.** An instrument used to conduct electrodialysis.

**Electrodisintegration.** The breakup of a nucleus into two or more fragments as a result of bombardment by electrons.

**Electroforming.** An electrolytic plating process for manufacturing metal parts. A mold of the object to be reproduced is made in a soft metal or in wax (by impression). The mold surface is made conducting by coating with graphite. Some suitable metal is then deposited electrolytically on the mold surface. This mold is then (in most cases) a negative of the object to be produced. Other industrial applications are phonograph records, plastic tile, ducting, tubing, etc.

**Electrogravimetry.** Electrodeposition analysis in which the quantities of metals deposited may be determined by weighing a suitable electrode before and after deposition.

**Electrohydrodynamic Ionization Mass Spectroscopy.** A technique for analysis of non-volatile molecules in which the non-volatile material is dissolved in a volatile solvent with a high dielectric constant such as glycerol, and high electric-field gradients at the surface a droplets of the liquid solution induce ion emission.

**Electrokinetic Phenomena.** The phenomena associated with movement of charged particles through a continuous medium or



with the movement of a continuous medium over a charged surface.

**"Electroless" Coating.** A protective coating of copper, cobalt, nickel, gold, or palladium deposited in a bath without application of an electric current *i.e.*, by chemical reduction.

**Electroluminescence.** Luminescence generated in crystals by electric fields or currents in the absence of bombardment or other means of excitation. It is a solid-state phenomenon involving p and n-type semiconductors, and is observed in many crystalline substances, especially silicon carbide, zinc sulfide, gallium arsenide, as well as in silicon, germanium and diamond.

**Electrolysis.** Decomposition of water and other inorganic compounds in aqueous solution by means of an electric current, the extent being proportional to the quantity of electricity passing through the solution. The positive and negative ions formed are carried by the current to the oppositely charged electrodes, where they are collected (if wanted) or released (if unwanted). Metallic ions deposited on the electrode form a coating. A simple electrolysis is the separation of water into oxygen and hydrogen; this is one method of producing hydrogen. Somewhat more complicated is electrolysis of brine to chlorine and sodium hydroxide; this is carried out in electrolytic cells of the diaphragm or mercury type, with water taking part in the reaction. In electroplating, metal salts dissociate into their constituent ions, the positively charged metal ions coating the cathode. There are a number of variations of this process (electrodeposition, electrocoating, electroforming).

**Electrolyte.** A substance that will provide ionic conductivity when dissolved in water or when in contact with it; such compounds may be either solid or liquid. Familiar types are sulfuric acid and sodium chloride, which ionize in solution. A recently developed solid electrolyte, used originally in fuel cells, is a polymer of perfluorinated sulfonic acid used as the core of a water electrolysis cell for production of hydrogen and oxygen. When saturated with water it has high conductivity. The most

common application of electrolytes is in electroplating of metals, in which dissolved (ionized) metal salts are the electrolytes.

**Electrolyte Acid.** Legal label name for battery acid.

**Electrolytic Cell.** An electrochemical device in which electrolysis occurs when an electric current is passed through it. Ionizable compounds dissociate in the aqueous solution with which the electrodes are in contact. Such cells are of two types :

- (1) the diaphragm cell, which has two compartments separated by a porous membrane, and
- (2) the mercury cell, in which mercury is the cathode. The anodes of both types have long been made of graphite; because this decomposes rapidly as electrolysis progresses, they are being replaced with dimensionally stable types consisting of titanium coated with oxides of ruthenium and other rare metals, which are also much more efficient. In electrolysis of sodium chloride, the current causes chloride ion to migrate to the anode, where it is collected as chlorine gas; sodium hydroxide and hydrogen are also formed, the hydrogen being discharged. The overall cell reaction is :  $2\text{NaCl} + 2\text{H}_2\text{O} \longrightarrow \text{H}_2 + \text{Cl}_2 + 2\text{NaOH}$ . This principle is applied in the electroplating of metals, electrodeposition of colloids, and similar processes.

**Electrolysis.** A method by which chemical reactions are carried out by passage of electric current through a solution of an electrolyte or through a molten salt.

**Electrolyte.** A chemical compound which when molten or dissolved in certain solvents, usually water, will conduct an electric current.

**Electrolytic Analysis.** Basic electrochemical technique for quantitative analysis of conducting solutions containing oxidizable or reducible material; measurement is based on the weight of material plated out onto the electrode.

**Electrolytic Cell.** A cell consisting of electrodes immersed in an electrolyte solution, for carrying out electrolysis.

**Electrolytic Conductance.** The transport of electric charges, under electric potential differences, by charged particles (called ions) of atomic or larger size.

**Electrolytic Conductivity.** The conductivity of a medium in which the transport of electric charges, under electric potential differences, is by particles of atomic or larger size.

**Electrolytic Potential.** Difference in potential between an electrode and the immediately adjacent electrolyte, expressed in terms of some standard electrode difference.

**Electrolytic Process.** An electrochemical process involving the principles of electrolysis, especially as relating to the separation and deposition of metals.

**Electrolytic Separation.** Separation of isotopes by electrolysis, based on differing rates of discharge at the electrode of ions of different isotopes.

**Electrolytic Solution.** A solution made up of a solvent and an ionically dissociated solute; it will conduct electricity, and ions can be separated from the solution by deposition on an electrically charged electrode.

**Electromigration.** A process used to separate isotopes or ionic species by the differences in their ionic mobilities in an electric field.

**Electromodulation.** Modulation spectroscopy in which changes in transmission or reflection spectra induced by a perturbing electric field are measured.

**Electromotive Force.** 1. The difference in electric potential that exists between two dissimilar electrodes immersed in the same electrolyte or otherwise connected by ionic conductors. 2. The resultant of the relative electrode potential of the two dissimilar electrodes at which electrochemical reactions occur. Abbreviated emf. Also known as electromotance.

**Electromotive Series.** See displacement series; electrochemical series.

**Electron Capture Detector.** Extremely sensitive gas chromatography detector that is a modification of the argon ionization

detector, with conditions adjusted to favor the formation of negative ions.

**Electronegative Potential.** Potential of an electrode expressed as negative with respect to the hydrogen electrode.

**Electron Energy Level.** A quantum-mechanical concept for energy levels of electrons about the nucleus; electron energies are functions of each particular atomic species.

**Electron Energy Loss Spectroscopy.** A technique for studying atoms, molecules, or solids in which a substance is bombarded with monochromatic electrons, and the energies of scattered electrons are measured to determine the distribution of energy loss.

**Electronic Absorption Spectrum.** Spectrum resulting from absorption of electromagnetic radiation by atoms, ions, and molecules due to excitations of their electrons.

**Electronic Angular Momentum.** The total angular momentum associated with the orbital motion of the spins of all the electrons of an atom.

**Electronic Band Spectrum.** Bands of spectral lines associated with a change of electronic state of a molecule; each band corresponds to certain vibrational energies in the initial and final states and consists of numerous rotational lines.

**Electronic Emission Spectrum.** Spectrum resulting from emission of electromagnetic radiation by atoms, ions, and molecules following excitations of their electrons.

**Electronic Energy Curve.** A graph of the energy of a diatomic molecule in a given electronic state as a function of the distance between the nuclei of the atoms.

**Electronic Magnetic Moment.** The total magnetic dipole moment associated with the orbital motion of all the electrons of an atom and the electron spins; opposed to nuclear magnetic moment.

**Electronic Spectrum.** Spectrum resulting from emission or absorption of electromagnetic radiation during changes in the electron

configuration of atoms, ions, or molecules, as opposed to vibrational, rotational, fine-structure, or hyperfine spectra.

**Electron Magnetic Moment.** The magnetic dipole moment which an electron possesses by virtue of its spin. Also known as electron dipole moment.

**Electron Microscope.** A microscope in which the source of illumination is a stream of electrons emanating from a tungsten cathode in a high vacuum and accelerated by a strong electric impulse (300 kilovolts). The electrons are focused by a series of magnetic fields which function as lenses, in the same way as glass affects waves of visible light, *i.e.*, the electron stream curves as it passes through the magnetic field. Such lenses were developed in Germany by Busch, Knoll, and Ruska in the 1930's, and were adapted to microscopy by Zworykin and Hillier at the RCA Laboratories in the early 1940's, when the first commercial instruments were produced. The electron microscope is characterized by extremely high resolving power due to the ultra-short wavelength of electronic radiation—a small fraction of an Angstrom unit. Resolution of less than 5 Angstrom units is possible, which permits determination of the structure of macromolecule (DNA) and even observation of large atoms (uranium).

Two kinds of electron microscopes are in general use : the transmission type, in which the electrons penetrate the specimen, and the scanning type, introduced in 1970, in which the electrons, condensed to a fine beam, repeatedly traverse the surface of the specimen, producing a three-dimensional contour effect by means of secondary electrons emanating from the specimen itself. Pictures of astonishing accuracy have been obtained, especially of surface structures, a matter of great importance in the study of catalysis and other critical phenomena in both industry and the biological sciences. A unique combination of these techniques is the scanning transmission electron microscope (STEM) by means of which colored motion pictures of uranium atoms on a thin-film carbon substrate have been obtained. See also : optical

micro-scope; resolving power; ultra-microscope; field-ion microscope.

**Electron Paramagnetic Resonance. (EPR)** A method of spectroscopic analysis similar to nuclear magnetic resonance except that microwave radiation is employed instead of radiofrequencies. It is used for studying free radicals, crystal centers, transition elements and structures involving unpaired electrons.

**Electron Nuclear Double Resonance.** A type of electron paramagnetic resonance (EPR) spectroscopy permitting greatly enhanced resolution, in which a material is simultaneously irradiated at one of its EPR frequencies and by a second oscillatory field whose frequency is swept over the range of nuclear frequencies. Abbreviated ENDOR.

**Electron Number.** The number of electrons in an ion or atom.

**Electron Probe Microanalysis.** A technique in analytical chemistry in which a finely focused beam of electrons is used to excite an x-ray spectrum characteristic of the elements in the sample; can be used with samples as small as  $10^{-11}$  cubic centimeter.

**Electron Spectroscopy.** The study of the energy spectra of photoelectrons or Auger electrons emitted from a substance upon bombardment by electromagnetic radiation, electrons, or ions; used to investigate atomic, molecular, or solidstate structure, and in chemical analysis.

**Electron Spectrum.** Visual display, photograph, or graphical plot of the intensity of electrons emitted from a substance bombarded by x-rays or other radiation as a function of the kinetic energy of the electrons.

**Electron Spin Resonance E.S.C.** In the absence of any external fields, all spatial orientations of the electron spin are equally probable. On the application of a magnetic field. However, the spins are aligned either parallel or antiparallel to the direction of the magnetic field vector. The energy difference between these two states is  $g\beta H$  where  $g$  is the Lande factor,  $\beta$  is the Bohemageton and  $H$  is the strength of the

applied magnetic field. Boltzmann's law governs the distribution of spins between the two states, and at normal temperatures there is a slight excess in the lower energy state.

In an electron spin resonance spectrometer, transitions between the two states are brought about by the application of the quantum of energy  $h\nu$  which is equal to  $g\beta H$ . The resonance condition is defined when  $h\nu = g\beta H$  and this is achieved experimentally by varying  $H$  keeping the frequency ( $\nu$ ) constant. E.s.r. spectroscopy is used extensively in chemistry in the identification and elucidation of structures of radicals.

**Electron-volt (eV).** An extremely small unit used in measuring the energy of electrons and other nuclear constituents. It is the energy developed by an electron in falling through a potential difference of 1 volt, equivalent to  $1.6 \times 10^{-19}$  joule. The rupture of a carbon-to-carbon bond has been calculated to yield about 5 eV.

**Electroosmosis.** The movement in an electric field of liquid with respect to colloidal particles immobilized in a porous diaphragm or a single capillary tube.

**Electropherography.** See electrochromatography.

**Electrophoresis.** Migration of suspended or colloidal particles in a liquid such as rubber latex, due to the effect of potential difference across immersed electrodes. The migration is toward electrodes of charge opposite to that of the particles. Most solids, being negatively charged, migrates to the anode, the exception being basic dyes, hydroxide sols, and colloids which have adsorbed positive ions, all of which are positively charged and migrate to the cathode. Migrating particles lose their charge at the electrode, and generally agglomerate around it. Clay suspensions can be filtered by means of forced flow electrophoresis.

Electrophoresis is important in the study of proteins because the molecules of such materials act like colloidal particles and their charge is positive or negative according to whether the surrounding solution is acidic or basic. Thus, the

acidity of the solution can be used to control the direction which a protein moves upon electrophoresis.

**Electrophoretic Effect.** Retarding effect on the characteristic motion of an ion in an electrolytic solution subjected to a potential gradient, which results from motion in the opposite direction by the ion atmosphere.

**Electrophoretic Mobility.** A characteristic of living cells in suspension and biological compounds (proteins) in solution to travel in an electric field to the positive or negative electrode, because of the charge on these substances.

**Electropositive Potential.** Potential of an electrode expressed as positive with respect to the hydrogen electrode.

**Electroreflectance.** Electromodulation in which reflection spectra are studied. Abbreviated ER.

**Elgin Extractor.** Spray-tower, multistage, counterflow extractor in which the diameter of the base section is expanded to eliminate flow restriction at the light-liquid distribution location.

**Eluant.** A liquid used to extract one material from another, as in chromatography.

**Eluate.** The solution that results from the elution process.

**Elution.** The removal of adsorbed species from a porous bed or chromatographic column by means of a stream of liquid or gas.

**Elutriation.** The process of separating a material into fractions of various sizes by allowing it to settle against an upward moving stream of fluid, usually air or water. The individual particles will settle through the fluid at a definite velocity depending on size, density and a number of other factors. Given a material of uniform density there will be, under any given set of conditions, a certain particle size at which the rate of descent is equal to the velocity of the fluid stream. All particles larger than this will sink to the bottom of the elutriator, and all smaller particles will pass out of the vessel.



with the fluid stream and may be recovered by some suitable mean.

**Emission Flame Photometry.** A form of flame photometry in which a sample solution to be analyzed is aspirated into a hydrogen-oxygen or acetylene-oxygen flame; the line emission spectrum is formed, and the line or band of interest is isolated with a monochromator and its intensity measured photoelectrically.

**Emission Lines.** Spectral lines resulting from emission of electromagnetic radiation by atoms, ions, or molecules during changes from excited states to states of lower energy.

**Emission Spectrometer.** A spectrometer that measures per cent concentrations of preselected elements in samples of metals and other materials; when the sample is vaporized by an electric spark or arc, the characteristic wavelengths of light emitted by each element are measured with a diffraction grating and an array of photodetectors.

**Emission Spectroscopy.** Study of the composition of substances and identification of elements by observation of the wavelengths of radiation they emit as they return to a normal state after excitation by an external energy source. When atoms or molecules are excited by energy input from an arc, spark, or flame, they respond in a characteristic manner; their identity and composition are signaled by the wavelengths of incident light they emit. The spectra of elements are in the form of lines of distinctive color, such as the yellow sodium D line of sodium; those of molecules are groups of lines called bands. The number of lines present in an emission spectrum depends on the number and position of the outermost electrons and the degree of excitation of the atoms. The first application of emission spectra was identification of sodium in the solar spectrum (1814).

**Emission Spectrum.** Electromagnetic spectrum produced when radiations from any emitting source, excited by any of various forms of energy, are dispersed.

**Empirical Formula.** A chemical formula indicating the variety and

relative proportions of the atoms in a molecule but not showing the manner in which they are linked together.

**Emulsification Test.** Standard laboratory procedure for evaluating the resistance of insulating oils, turbine oils, and other lubricating oils to emulsification.

**ENDOR.** See electron nuclear double resonance.

**Endotherm.** In differential thermal analysis, a graph of the temperature difference between a sample compound and a thermally inert reference compound (commonly aluminium oxide) as the substances are simultaneously heated to elevated temperatures at a predetermined rate, and the sample compound undergoes endothermal or exothermal processes.

**Endothermic.** Pertaining to a reaction which absorbs heat. Also known as endoergic.

**End Point.** 1. In the distillation analysis of crude petroleum and its products, the highest reading of a thermometer when a specified proportion of the liquid has boiled off. Also known as final boiling point. 2. That stage in the titration at which an effect, such as a color change, occurs, indicating that a desired point in the titration has been reached.

**End Point, Final Boiling Point.** In a laboratory distillation the maximum thermometer reading obtained in the test and usually coinciding with evaporation of all the liquid in the flask, but see decomposition point.

**Engler Distillation Test.** A standard test for determination of the volatility characteristics of a gasoline by the measurement of the gasoline distilled at various specific temperatures.

**Engler Flask.** A standardized flask of 100-milliliter volume used in the Engler distillation test.

**English Degree.** A unit of water hardness, equal to 1 part calcium carbonate to 70,000 parts water; equivalent to 1 grain of calcium carbonate per gallon of water. Also known as Clark degree.

**Enhanced Spectral Line.** A spectral line of a very hot source, such as a spark, whose intensity is much greater than that of a line in a flame or arc spectrum. Also known as enhanced line.

**Enriching Column.** The portion of a countercurrent extractor (liquid-liquid extraction or vapor-liquid distillation) above the feed point in which an upward-moving, product-rich stream from the stripping column is further purified by countercurrent contact with a downward-flowing reflux stream from the overhead product-recovery vessel.

**Enthalpimetric Analysis.** Generic designation for a group of modern thermochemical methodologies such as thermometric enthalpy titrations which rely on monitoring the temperature changes produced in adiabatic calorimeters by heats of reaction occurring in solution; in contradistinction, classical methods of thermoanalysis such as thermogravimetry focus primarily on changes occurring in solid samples in response to externally imposed programmed alterations in temperature.

**Entrainer.** An additive that forms an azeotrope with one component of a liquid mixture to aid in otherwise difficult separations by distillation as in azeotropic distillation.

**Entrainment.** A process in which the liquid boils so violently that suspended droplets of liquid are carried in the escaping vapor.

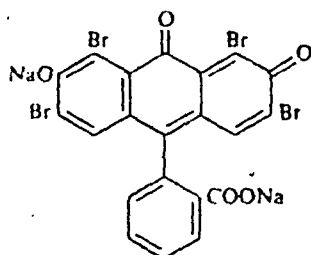
**Entrance Slit.** Narrow slit through which passes the light entering a spectrometer.

**Entropy of Activation.** The difference in entropy between the activated complex in a chemical reaction and the reactants.

**Entropy of Mixing.** After mixing substances, the difference between the entropy of the mixture and the sum of the entropies of the components of the mixture.

**Eosin.** The sodium salt of tetrabromofluorescein. The free acid, eosin is a yellow-red substance; m.p. 295—296°C. Prepared.

by the direct bromination of fluorescein. The dye is red, b shows a brilliant fluorescence in ultra-violet light. Spirit-solub



eosins are the methyl and ethyl-esters. Eosin is used as a co constituent of red inks, and as a stain for tissue slices. It has po light fastness.

**Equidensity Technique.** Interference microscopy technique utilizing the Sabattier effect in photographic emulsions; the equidensity lines (lines of equal density in a photographic emulsion) are produced by exactly superimposing a positive and a negative of the same interferogram, and making a copy; used to measure photographic film emulsion density.

**Equilibrium Constant.** A constant at a given temperature such that when a reversible chemical reaction  $cC + bB = gG + hH$  has reached equilibrium, the value of this constant  $K^\circ$  is equal to

$$\frac{a_G^g a_H^h}{a_C^c a_B^b}$$

where  $a_G$ ,  $a_H$ ,  $a_C$ , and  $a_B$  represent chemical activities of the species G, H, C, and B at equilibrium.

**Equilibrium Diagram.** A phase diagram of the equilibrium relationship between temperature, pressure, and composition in any system.

**Equilibrium Dialysis.** A technique used to determine the degree of ion bonding by protein; the protein, solution placed in a bag impermeable to protein but permeable to small ions, is immersed in a solution containing the diffusible ion whose binding is being studied; after equilibration of the ion across the membrane, the concentration of ion in the protein-free solution is determined; the concentration of ion in the protein solution

is determined by subtraction; if binding has occurred, the concentration of ion in the protein solution must be greater.

**Equilibrium Flash Vaporization.** Process in which a continuous liquid-mixture feed stream is partly vaporized in a column or vessel, with continuous withdrawal of vapor and liquid portions, the vapor and liquid in equilibrium. Also known as continuous equilibrium vaporization; simple continuous distillation.

**Equilibrium Moisture Content.** The moisture content in a hygroscopic material that is being dried by contact with air at constant temperature and humidity when a definite, fixed (equilibrium) moisture content in the solid is reached.

**Equilibrium Potential.** A point in which forward and reverse reaction rates are equal in an electrolytic solution, thereby establishing the potential of an electrode.

**Equilibrium Prism.** Three-dimensional (solid) diagram for multicomponent mixtures to show the effects of composition changes on some key property, such as freezing point.

**Equilibrium Still.** Recirculating distillation apparatus (no product withdrawal) used to determine vapor-liquid equilibria data.

**Equilibrium Vaporization Ratio.** In a liquid-vapor equilibrium mixture, the ratio of the mole fraction of a component in the vapor phase ( $y$ ) to the mole fraction of the same component in the liquid phase ( $x$ ), or  $y/x = K$  (the  $K$  factor). Also known as equilibrium ratio.

**Equivalence Point.** The stage in a titration when the reactants and products are present in equivalent amounts according to the stoichiometry of the reaction. This may not correspond exactly to the end point.

**Equivalent Conductance.** Property of an electrolyte, equal to the specific conductance divided by the number of gram equivalents of solute per cubic centimeter of solvent.

**Equivalent Weight (combining weight).** The weight of an element that combines chemically with 8 grams of oxygen or its

## Errors

equivalent. Since 8 grams of oxygen combines with 1.0 grams of hydrogen, the latter is considered equivalent to 8 grams of oxygen. When 8 grams is selected for the combining weight of oxygen, no element has a combining weight value less than 1. The equivalent weight of an acid is the weight that contains one atomic weight of acidic hydrogen, *i.e.*, the hydrogen that reacts during neutralization of an acid with base. The equivalent weight of a base or hydroxide is the weight that will react with an equivalent weight of an acid. Equivalent weights of other substances are defined in a similar manner.

**Equivalent Weight.** The number of parts by weight of an element or compound which will combine with or replace, directly or indirectly, 1.008 parts by weight of hydrogen, 8.00 parts by weight of oxygen, or the equivalent weight of any other element or compound.

**Equiviscous Temperature.** A measure of viscosity used in the petroleum industry, equal to the temperature in degrees Celsius at which the viscosity of tar is 50 seconds as measured in a standard tar efflux viscometer. Abbreviated EVT.

**Erlenmeyer Flask.** A useful type of laboratory glassware; it is a conical open container whose dimensions are, for example, about 6 inches tall, with a relatively narrow neck section about 1 inch in diameter and 2 inches long, below which the container becomes cone-shaped. The bottom is flat. It is used in numerous experiments involving liquids, especially titrations and extractive testing. It was named after its inventor, Erlenmeyer, a German chemist.

**Errors.** The errors which come across in analysis can be broadly classified into two major groups as :

- (1) determinate errors,
- (2) indeterminate errors. Determinate errors are errors which can be measured and accounted for while indeterminate errors are the random errors which cannot be easily located. Determinate errors are classified into four groups :

- (1) Instrumental errors,
- (2) Method errors,
- (3) Operational errors,
- (4) Personal or human errors.

**Instrumental errors :** Instrumental errors arise due to faults in the instruments, tools used in the analysis. For example poor calibration of glass-ware, impurities in chemicals used, wrong balance weights, voltage fluctuations in using electronic instruments cause such errors in the analysis.

**Method errors :** Method errors arise due to a reaction not going to completion or due to some side reactions taking place. Coprecipitation, simultaneous precipitations, and post-precipitations are some other causes which give rise to method errors in gravimetric estimations.

**Operational errors :** Operational errors arise due to insufficient knowledge of the instrument used and not taking the necessary precautions in using the instrument. Lack of experience of the analyst, introduction of certain impurities due to negligence, loss due to splitting of sample, weighing the materials under wrong conditions, excess use of indicators in titrations cause operational errors in analysis.

**Personal errors or Human errors :** Personal errors arise as a consequence of faulty ideas, improper technique, carelessness, ignorance and physical limitations, of the experimenter. Certain misconceived ideas in measurement, prejudice or bias of unreasoned and unfair fixed ideas in analysis, physical limitations such as colour blindness, cause personal errors.

Indeterminate errors are classified into constant and proportionate errors.

**Constant and Proportionate errors :** Determinate errors may be due to constant or proportionate errors. Constant errors are those which are independent of the sample size and proportionate errors are those which increase in direct proportion to sample size.

### *Ethylenediaminetetraacetic*

**Eschka Mixture.** A mixture of two parts magnesium oxide and one part anhydrous sodium carbonate; used as a fusion mixture for determining sulfur in coal.

**Eschweller-Clarke Modification.** A modification of the Leuckart reaction, involving reductive alkylation of ammonia or amines (except tertiary amines) by formaldehyde and formic acid.

**Ethyl Bromide.**  $C_2H_5Br$ . A colorless liquid, boiling at  $39^\circ C$ ; used as a refrigerant and in organic synthesis. Also known as bromic ether; bromoethane.

**Ethyl Chloride**  $C_2H_5Cl$ . A colorless gas, liquefying at  $12.2^\circ$ , slightly soluble in water; used as a solvent, in medicine, and as an intermediate. Also known as chloroethane; hydrochloric ether; monochloroethane; muriatic ether.

**Ethylenediaminetetraacetic Acid.** (EDTA; ethylenebisiminodiacetic acid; ethylenedinitrilotetraacetic acid)  $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$ . An organic chelating agent.

**Properties :** Colorless crystals, decomposing at  $240^\circ C$ . Slightly soluble in water; insoluble in common organic solvents; neutralized by alkali metal hydroxides to form a series of water-soluble salts containing from one to four alkali metal cations. Low toxicity.

**Derivation :**

- Addition of sodium cyanide and formaldehyde to a basic solution of ethylenediamine (forms the tetrasodium salt);
- heating tetrahydroxyethylethylenediamine with sodium or potassium hydroxide with cadmium oxide catalyst.

**Uses :** Detergents, liquid soaps, shampoos, agricultural chemical sprays; metal cleaning and plating; metal chelating agent; treatment of chlorosis; decontamination of radioactive surfaces; metal deactivator in vegetable oils, oil emulsions pharmaceutical products, etc; anticoagulant of blood; eluting agent in ion exchange; to remove insoluble deposits of calcium and magnesium soaps; in textiles to improve dyeing scouring, and detergent operations; antioxidant; clarification of liquids; analytical chemistry; spectrophotometric titration aid in reducing blood cholesterol; in medicine to treat lead poisoning and calcinosis; food additive (preservative).



Note : A number of salts of EDTA are available with uses identical or similar to the acid. The U.S.P. salts are called edetates (calcium disodium, disodium edetates); others are usually abbreviated to EDTA (tetrasodium, trisodium EDTA). Other salts, known chiefly under trademarked names, are the sodium ferric, dihydrogen ferrous, and a range of disodium salts with magnesium, divalent cobalt, manganese, copper, zinc and nickel.

**Ethylenediaminetetraacetoneitrile. (EDTAN)**



Properties : White crystalline solid; melting range 126-132°C; bulk density 48.4 lb/cu ft. Slightly soluble in water; soluble in acetone.

Hazard : Toxic by ingestion and inhalation.

Uses : Chelating agent and intermediate.

**Eutectic.** The lowest melting point of an alloy or solution of two or more substances (usually metals) that is obtainable by varying the percentage of the components. Eutectic alloys are relatively few; they are the particular alloys that have definite and minimum melting points compared with other combinations of the same metals.

**Eutectic Point.** The point in the constitutional diagram indicating the composition and temperature of the lowest melting point of a eutectic.

**Eutectic System.** The particular composition and temperature of materials at the eutectic point.

**Eutectic Temperature.** The temperature at the lowest melting point of a eutectic.

**Eutectogenic System.** A multicomponent liquid solid mixture in which pure solid phases of each component are in equilibrium with the remaining liquid mixture at a specific (usually minimum) temperature for a given composition, that is, the eutectic point.

**Eutectoid.** The point in an equilibrium diagram for a solid solution at which the solution on cooling is converted to a mixture of solids.

## *Excitation Spectrum*

**Evaporator.** A device used to vaporize part or all of the solvent from a solution; the valuable product is usually either a solid or concentrated solution of the solute.

**Exchange Adsorption.** Ion exchange process in which the adsorbent phase contains (or consists of) two adsorbable components which together entirely saturate the surfaces of the adsorbent.

**Exchange Broadening.** The broadening of a spectral line by a type of chemical or spin exchange process which limits the lifetime of the absorbing or emitting species and produces broadening via the Heisenberg uncertainty principle.

**Exchange Narrowing.** The phenomenon in which, when a spectral line is split and thereby broadened by some variable perturbation, the broadening may be narrowed by a dynamic process that exchanges different values of the perturbation.

**Excitation Curve.** A curve showing the relative yield of a spectral nuclear reaction as a function of the energy of the incident particles or photons. Also known as excitation function.

### **Excitation Function**

1. The cross section for an incident electron to excite an atom to a particular excited state expressed as a function of the electron energy.
2. See excitation curve.

**Excitation Index.** In emission spectroscopy, the ratio of intensities of a pair of extremely nonhomologous spectra lines; used to provide a sensitive indication of variation in excitation conditions.

**Excitation Purity.** The ratio of the departure of the chromaticity of a specified color to that of the reference source, measured on a chromaticity diagram; used as a guide of the wavelength spectrum color needed to be mixed with a reference color to give the specified color.

**Excitation Spectrum.** The graph of luminous efficiency per unit energy of the exciting light absorbed by a photoluminescent body versus the frequency of the exciting light.

**Excited State.** A higher than normal energy level (vibrational frequency) of the electrons of an atom, radical, or molecule resulting from absorption of photons (quanta) from a radiation source (arc, flame, spark, etc.) in any wavelength of the electromagnetic spectrum. X-ray, ultraviolet, visible, infrared, microwave, and radiofrequencies are used for excitation in various types of spectroscopy. When the energizing source is removed or discontinued the atom or molecule returns to its normal or stable state either by emitting the absorbed photons or by transferring the energy to other atoms or molecules. The increased vibrational activity of the atom or molecule yields line or band spectra characteristic of its structure, thus permitting identification. Photochemical reactions are induced by excited chemical entities, which are also responsible for the phenomena of luminescence (phosphorescence and fluorescence).

**Exciting Line.** The frequency of electromagnetic radiation, that is, the spectral line from a noncontinuous source, which is absorbed by a system in connection with some particular process.

**Exciton.** An energetic entity induced in semiconductor crystals by incident radiation and occurring in the field area between a hole and its displaced electron. It is conceived as behaving like an uncharged particle having quantum-mechanical properties.

**Exergonic.** Of or pertaining to a biochemical reaction in which the end products possess less free energy than the starting materials; usually associated with catabolism.

**Exhaustion Point.** In an ion-exchange process, the state of an adsorbent at which it no longer can produce a useful ion exchange.

**Explosive Limits.** The range of concentration of a flammable gas or vapor (% by volume in air) in which explosion can occur upon ignition in a confined area. Explosive limits for some common substances are :

	Lower (%)	Upper (%)
carbon disulfide	1	50

benzene	1.5	8
methane	5	15
butadiene	2	11.5
butane	1.9	8.5
propane	2.4	9.5
natural gas	3.8	17
hydrogen	4	75
acetylene	2.5	80

**Exposure Testing.** Determination of the degradation of a material by exposing samples to an environment selected for its adverse effect. Materials most frequently tested are paints, metals and alloys, rubber, and plastics. An area frequently chosen is the coast of southern Florida, where the combination of high temperature, strong sunlight, salt air, and moisture is particularly severe, especially as regards metal corrosion. Burial of metals in acid soils for long periods of time and immersion of impregnated wood samples in sea water are other exposure testing techniques.

**Expression.** Separation of liquid from a two-phase solid-liquid system by compression under conditions that permit liquid to escape while the solid is retained between the compressing surfaces. Also known as mechanical expression.

**Extensive Property.** A noninherent property of a system, such as volume or internal energy, that changes with the quantity of material in the system; the quantitative value equals the sum of the values of the property for the individual constituents.

**External Circuit.** All connecting wires, devices, and current sources which achieve desired conditions within an electrolytic cell.

**External Indicators.** Titration of Iron (II) with standard potassium dichromate solution using potassium hexacyanoferrate (III),  $K_3Fe(CN)_6$  as an external indicator is the most common example. As the equivalence point reaches, a drop of the solution is brought in contact with the freshly prepared indicator solution on a spot plate. When there is no blue colouration it shows the end point has reached.

**Extinction.** See absorbance.

**Extinction Coefficient.** See absorptivity.

**Extract.** Material separated from liquid or solid mixture by a solvent.

**Extractant.** The liquid used to remove a solute from another liquid.

**Extraction.** A method of separation in which a solid or solution is contacted with a liquid solvent (the two being essential mutually insoluble) to transfer one or more components into the solvent.

**Extraction Column.** Vertical-process vessel in which a desired product is separated from a liquid by countercurrent contact with a solvent in which the desired product is preferentially soluble.

**Extractive Distillation.** If two substances have boiling points close together, or form an azeotrope, separation by normal fractionation is not feasible. Extractive distillation is a method whereby a third substance is added which decreases the volatility of one compound relative to the other, and makes separation by distillation possible.

The third substance or solvent is considerably less volatile than the other two, and is introduced above the feed near the top of the column. From the top of the column one of the substances is obtained in a pure state while the other, mixed with the solvent, is taken from the bottom of the column. A second column is used to separate the other substance from the solvent, the latter being recycled.

Extractive distillation processes are of considerable industrial importance. *E.g.* the separation of *n*-butane from isobutane using propanone or acrylonitrile as the solvent, and benzene from alkanes using phenol as solvent.

**Extractor.** An apparatus for solvent-contact with liquids or solids for removal of specified components.

**Extreme Narrowing Approximation.** A mathematical approximation in the theory of spectral-line shapes to the effect that the exchange narrowing of a perturbation is complete.

# F

**Falling Drop Analysis.** A microanalytical procedure for the determination of  $D_2O$  content of  $H_2O$  and inter alia the atom. % deuterium content of organic substances which can be combusted to water. 100 mol. %  $D_2O$  has a density approximately 10% greater than that of 100 mol. %  $H_2O$  and the densities of mixtures of intermediate composition fall on a smooth curve between these extremes. The rate of fall of  $1\ \mu l$  droplets of water through heterogeneous organic solvent mixtures allows estimation of isotopic content with an accuracy of 10 p.p.m.

Mass spectrometry is a more accurate and convenient technique which has superseded the falling drop method.

**Faraday.** The quantity of electricity that can deposit (or dissolve) one gram-equivalent weight of a substances during electrolysis (about 96,500 coulombs).

**Faraday's Laws of Electrolysis**

1. The amount of any substance dissolved or deposited in electrolysis is proportional to the total electric charge passed.
2. The amount of different substances dissolved or desposited by the passage of the same electric charge are proportional to their equivalent weights.

**Fast Chemical Reaction.** A reaction with a half-life of milliseconds or less; such reactions occur so rapidly that special experimental techniques are required to observe their rate.

**Fast-neutron Spectrometry.** Neutron spectrometry in which nuclear reactions are produced by or yield fast neutrons; such reactions are more varied than in the slow-neutron case.

**Fat.** Any of the glyceryl esters of fatty acids which form a class of neutral organic compounds.

**FD & C Colors.** A series of colorants permitted in food products, marking inks, etc.

Among the more important are the following :

**Blue No. 1 :** Disodium salt of 4-((N-ethyl-p-sulfobenzylamino)—phenyl)—(2-sulfoniumphenyl)—methylene)-(1-(N-ethyl-N-p-sulfobenzyl)- $\Delta^{2,5}$ -cyclohexadienimine).

**Blue No. 2 :** Disodium of 5,5'-indigotindisulfonic acid.

**Green No. 3 :** Disodium salt of 4-((4-(N-ethyl-p-sulfobenzylamino)-phenyl-(4-hydroxy-2-sulfonium-phenyl)-methylene-(1-(N-ethyl-N-p-sulfobenzyl)- $\Delta^{2,5}$ -cyclohexadienimine).

**Green No. 6 :** 1, 4-di-para-toluidinoanthraquinone.

**Red No. 2 :** Trisodium salt of 1- 4-sulfo-1-naphthyl-azo)-2-naphthol-3, 6-disulfonic acid. Formerly, the largest-volume food color in commercial use. A suspected carcinogen. Use prohibited by FDA. Red No. 40 is permissible substitute.

**Red No. 3:** Disodium salt of 9-o-carboxyphenyl 6-hydroxy-2, 4, 5, 7-tetraiodo-3-isoxanthone (erythrosin).

**Red No. 4 :** Disodium salt of 2-(5-sulfo-2, 4-xylylazo)-naphthyl-4-sulfonic acid. Use in foods prohibited by FDA.

**Violet No. 1 :** Monosodium salt of 4-((4-N-ethyl-p-sulfobenzylamino)—phenyl)—(4(N-ethyl- p-sulfoium-benzylamino)—pheney)-methylene)-(N, N, dimethyl- $\Delta^{2,5}$ -cyclohexadienimine). Use prohibited by FDA in 1973 and by USDA in 1976.

**Yellow No. 5 :** Trisodium salt of 3-carboxy-5-hydroxy-1-p-sulfophenyl-4-sulfophenylazopyrazole.

**Yellow No. 6 :** Disodium salt of 1-p-sulfophenylaze-2-naphthol-6-sulfonic acid.

**Fehling's Reagent.** A solution of cupric sulfate, sodium potassium tartrate, and sodium hydroxide, used to test for the presence of reducing compounds such as sugars.

**Fenske-underwood Equation.** Equation in plate-to-plate distillation-column calculations relating the number of theoretical plates needed at total reflux to overall relative volatility and the liquid-vapor composition ratios on upper and lower plates. Also known as Fenske equation.

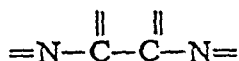
**Fermi Constant.** A universal constant, introduced in beta-disintegration theory, that expresses the strength of the interaction between the transforming nucleon and the electron-neutrino field.

**Fermi Resonance.** In a polyatomic molecule, the relationship of two vibrational levels that have in zero approximation nearly the same energy; they repel each other, and the eigenfunctions of the two states mix.

**Fermi Selection Rules.** Selection rules for beta decay in a Fermi transition; that is, there is no change in total angular momentum or parity of the nucleus in an allowed transition.

**Ferrocyanide.** A salt containing the radical  $\text{Fe}(\text{CN})_6^{4-}$ .

**Ferroin Chelation Group.** A functional group characteristic of heterocyclic ring nitrogen compounds :



Among such compounds are 2,2' bipyridine, 1, 10-phenanthroline, and the 2-pyridyl triazines. These provide a large number of terminal ( $=\text{C}-\text{H}$ ) groups in which the hydrogen can be replaced by many chemical groupings (carboxyl, hydroxyl, halogen, etc.). Thus synthesis of an almost endless number of substituted ferroin reactants is possible. About 200 such chelation reagents have been synthesized. Ferroin chelation chemicals in general form complex undissociated cations with divalent metal ions, e.g.,  $[(\text{C}_5\text{H}_5\text{N})_3\text{Fe}]^{+2}$ .

**Ferrous Ammonium Sulfate.** (Mohr's salt; iron ammonium sulfate)  $\text{Fe}(\text{SO}_4)(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ .



**Properties :** Light-green crystals. Soluble in water; insoluble in alcohol. Sp. gr. 1.865; dec. 100—110°C. Deliquescent; affected by light.

**Derivation :** By mixing solutions of ferrous sulfate and ammonium sulfate, followed by evaporation and subsequent crystallization.

**Uses :** Analytical chemistry; metallurgy.

**Feulgen Reaction.** An aldehyde specific reaction based on the formation of a purple-colored compound when aldehydes react with fuchsin-sulfuric acid; deoxyribonucleic acid gives this reaction after removal of its purine bases by acid hydrolysis; used as a nuclear stain.

**Field Desorption Mass Spectroscopy.** A technique for analysis of nonvolatile molecules in which a sample is deposited on a thin tungsten wire containing sharp microneedles of carbon on the surface; a voltage is applied to the wire, thus producing high electric-field gradients at the points of the needles, and moderate heating then causes desorption from the surface or molecular ions, which are focused into a mass spectrometer.

**Field Shift.** The portion of the mass shift produced by the change in the size and shape of the nuclear charge distribution when neutrons are added to the nucleus. Also known as volume shift.

**Film-development Chromatography.** Liquid-analysis chromatographic technique in which the stationary phase (adsorbent) is a strip or layer, as in paper or thin-layer chromatography.

**Filter Cake Washing.** An operation performed at the end of a filtration, in which residual liquid impurities are washed out of the cake by the flow of another liquid through the cake.

**Filter Flask.** A flask with a side arm to which a vacuum can be applied; usually filter flasks have heavy side walls to withstand high vacuum.

**Filter Leaf.** The frame or structure in a filter press that holds the filter cloth or other filter medium; a number of leaves in series usually comprises a filter press.

**Filter Media.** Almost any water-insoluble porous material having a reasonable degree of rigidity can serve as a filter. Sand is used in simple large-scale water filtration, the voids between the grains providing the porosity. In industrial operations cotton duck, woven wire cloth, nylon cloth and glass cloth are used. For laboratory work. Whatman filter paper, diatomaceous earth, and closely packed glass fibres are standard materials. Plastic membranes containing over a million pores per square inch are used in bacteriological filtration.

**Filtration Equipment.** The simplest industrial filter is the sand filter used for separating small amounts of solid from relatively large volumes of liquid. They consist of deep beds of graded sand, the finest material being on top of progressively coarser layers. Open beds may be used for water treatment while, for industrial use, sand may be contained in vessels with liquid forced through under pressure.

Leaf filters have a series of vertical leaves contained in horizontal, or sometimes vertical, cylindrical vessels, each leaf consisting of a metal or wire support covered by filter cloth or wire gauze. Slurry is normally fed under pressure, cake being built up on the leaves and filtrate draining through to the exit ports. Kelly, Sweetland and Vallez filters are examples of pressure leaf filters. The Moore filter is a leaf filter where vacuum is applied to the inside of the hollow leaves.

Rotary drum filters consist of horizontal drums with the perforated, cylindrical surface covered by filter cloth. They are rotated slowly with the bottom portion immersed in the slurry to be filtered. By means of an adjustable rotary valve and division of the drum into a number of sectors various areas of the cloth may be subjected to pressure or vacuum. This allows cake to be formed, washed and dried and finally

loosened by pressure for removal by a blade. The filters operate continuously and have a high capacity for their size. Internal drum filters or Dorco filters have the slurry inside the drum and are useful for rapidly-settling slurries.

Rotary vacuum disc filters are similar in principle to the rotary drum type. The filtering elements are disc mounted on a hollow, horizontal shaft which rotates with the lower half of the discs immersed in slurry. Each disc has sectors covered with individual filter bags and, on immersion in the slurry, a vacuum is applied via a rotary valve.

### **Filter Photometry**

1. Colorimetric analysis of solution colors with a filter applied to the eyepiece of a conventional colorimeter.
2. Inspection of a pair of Nessler tubes through a filter.

**Filter Press.** A relatively simple and widely-used type of plant for filtration under pressure. The chamber press comprises a number of plates having recessed, corrugated faces which are covered with filter cloths, the plates then being clamped together. Feed enters through a central channel and a solid cake is built up in each of the chambers, filtrate being discharged through an outlet in the body of the press. In the plate and frame press hollow, rectangular frames, usually 1.5—7.5 cm thick alternate with solid plates. Filter cloths are placed across each side of the frames, and plates and frames are clamped together. Slurry is fed into each frame and solid cake builds up within the frame, the filtrate flowing to discharge ports. Plate and frame presses have provision for washing the cake.

Filter presses operate at pressures up to about  $1800 \text{ kN/m}^2$  and so can be used for slow, difficult filtrations. They are simple, cheap, flexible and can be made from corrosion-resistant materials.

**Filter-presses Cell.** An electrolytic cell consisting of several units in series, as in a filter press, in which each electrode, except the

two end ones, acts as an anode on one side and a cathode on the other, and the space between electrodes is divided by porous asbestos diaphragms.

**Filter Spectrophotometer.** Spectrophotographic analyzer of spectral radiations in which a filter is used to isolate narrow portions of the spectrum.

**Filter Sand.** Sand used to separate sediment and suspended matter from water.

**Filtration.** The operation of separating suspended solids from a liquid (or gas) by forcing the mixture through a porous barrier. (See filter media). The construction and operation of the many kinds of industrial filtration equipment are too detailed to permit description. The most widely used types may be classified as follows :

- (1) gravity filters, used largely for water purification and consisting of thick beds of sand and gravel, which retain the flocculated impurities as the water passes through;
- (2) pressure filters of plate-and-frame or shell-and-leaf construction, which utilize filter cloths of coarse fabric as a separating medium;
- (3) vacuum or suction filters of the rotating drum or disk type, used on thick sludges and slurries;
- (4) edge filters;
- (5) clarification filters;
- (6) bag filters (dust collectors). See baghouse. Gel-filtration (q.v) is a chromatographic technique involving separation at the molecular level. For bacteriological filtration membranes having over a million pores per square inch are used, *e.g.*, collodion or synthetic film. Some types of virus will pass through such membranes and are thus known as filterable viruses.

**Fine Structure.** The splitting of spectral lines in atomic and molecular spectra caused by the spin angular momentum of the

electrons and the coupling of the spin to the orbital angular momentum.

**Fire Point.** The lowest temperature at which a volatile combustible substance vaporizes rapidly enough to form above its surface an air-vapour mixture which burns continuously when ignited by a small flame.

**First-order Reaction.** A chemical reaction in which the rate of decrease of concentration of component A with time is proportional to the concentration of A.

**First-order Spectrum.** A spectrum, produced by a diffraction grating, in which the difference in path length of light from adjacent slits is one wavelength.

**Fischer's Reagent.** A reagent used as a test for sugars. Preparation: 3 parts of sodium acetate and 2 parts of phenylhydrazine hydrochloride in 20 parts of water.

Note: Do not confuse with Karl Fischer reagent. (q.v.).

**Fission Spectrum.** The energy distribution of neutrons arising from fission.

**Fixed Carbon.** Solid, combustible residue remaining after removal of moisture, ash, and volatile materials from coal, coke, and bituminous materials; expressed as a percentage.

**Flame.** A hot, luminous reaction front (or wave) in a gaseous medium into which the reactants flow and out of which the products flow.

**Flame Emission Spectroscopy.** A flame photometry technique in which the solution containing the sample to be analyzed is optically excited in an oxyhydrogen or oxyacetylene flame.

**Flame Excitation** Use of a high-temperature flame (such as oxyacetylene) to excite spectra emission lines from alkali and alkaline-earth elements and metals.

**Flame-Front.** The region between the luminous zone and the dark zone of unburned gases which exists in all gas phase combustion reactions. Movement of the flame front is used to measure the burning velocity of gaseous mixtures.

**Flame Ionization Detector.** A device in which the measured change in conductivity of a standard flame (usually hydrogen) due to the insertion of another gas or vapor is used to detect the gas or vapor.

**Flame Photometer.** One of several types of instruments used in flame photometry, such as the emission flame photometer and the atomic absorption spectro-photometer, in each of which a solution of the chemical being analysed is vaporized: the spectral lines resulting from the light source going through the vapors enters a monochromator that selects the band or bands of interest.

**Flame Photometric Analysis.** Flame photometric analysis

Principle : Emission of a characteristic radiation by each element when introduced into a flame, and the correlation of the intensity of emission with concentration from the basis of flame photometry.

The flame photometer essentially consists of six parts :

- (1) Pressure regulators and flow meters for fuel gases.
- (2) Atomizer, (3) Burner, (4) Optical system, (5) Photo sensitive detector, (6) Recorder.

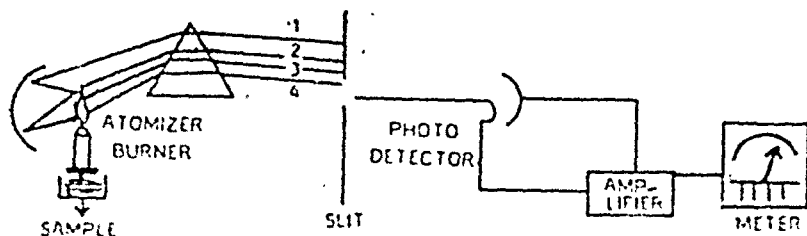


Fig.1

Pressure Regulators and Flow Meters : Suitable gauges. (A 101b gauge for fuel and 251b gauge for oxygen or air supply)

cuvette wall facing the exciting beam enable ultraviolet radiation below 320 nm to be used in exciting fluorescence. Photomultiplier tubes are used as detectors for measuring fluorescent radiations. To protect the photodetectors from reflected or scattered radiations secondary filters are placed before the detectors.

Since it is difficult to measure an absolute fluorescence intensity, measurements are usually made by reference to some arbitrarily chosen standard substance. A standard solution of the latter is placed in the instrument and the circuit balanced with the reading scale at any chosen setting. Without readjusting any circuit components, the standard solution is replaced by additional standard solutions of lesser concentration and lastly, the fluorescence of the solvent and cuvette alone is measured to establish a true zero concentration. Some fluorometers are equipped with a zero adjust circuit.

The applications of Fluorimetry are as follows :

(1) Fluorimetric methods require lower concentrations and hence are the most sensitive analytical techniques than spectrophotometric ones (2) Inorganic fluorimetric methods involve the formation of chelate and the measurement of its emission. (3) Non-transition metal ions which are colourless and tend to form chelates which are also colourless and for those compounds fluorimetry is widely used. (4) The most successful fluorometric reagents for cation analysis have aromatic structures with two or more donor functional groups that permit chelate formation with the metal ion. e.g. 8 hydroxy quinoline, benzoin, Alizarin and Flavanol. (5) The important applications of fluorimetry are in the analysis of food products, pharmaceuticals, clinical samples and natural products.

**Flame Photometry.** A branch of spectrochemical analysis in which samples in solution are excited to produce line emission spectra by introduction into a flame.

**Flame Spectrometry.** A procedure used to measure the spectra or to determine wavelengths emitted by flame-excited substances.

**Flame Spectrophotometry.** A method used to determine the intensity of radiations of various wavelengths in a spectrum emitted by a chemical inserted into a flame.

**Flame Spectrum.** An emission spectrum obtained by evaporating substances in a nonluminous flame.

**Flame Speed.** The rate at which combustion moves through an explosive mixture.

**Flash-back.** In gas burners having a stationary flame it is essential that the flame speed of the combustible mixture should be balanced by the velocity of the mixture in the burner tube or flame ports. If the flame speed is too high there will be flash-back of the flame onto the gas injector tube. This can be caused by an increase of air/fuel ratio.

**Flash Distillation.** Distillation in which an appreciable proportion of a liquid is quickly converted to vapor in such a way that the final vapor is in equilibrium with the final liquid. This method is now widely used for desalination of sea water.

**Flash Drum.** A facility, such as a tower, which receives the products of a preheater or heat exchanger to release pressure; volatile components are vaporized and separated for further fractionation.

**Flashing.** Vaporization of volatile liquids by either heat or vacuum.

**Flashing Flow.** The condition when a liquid at its boiling point flows through a heated conduit and is further heated to cause partial vaporization (flashing), with a resultant two-phase (vapor-liquid) flow.

**Flash Dry.** The rapid evaporation of moisture from a porous or granular solid by a sudden reduction in pressure or by placing the material in an updraft of warm air.



**Flash Photolysis.** A method of studying fast photochemical reactions in gas molecules; a powerful lamp is discharged in microsecond flashes near a reaction vessel holding the gas, and the products formed by the flash are observed spectroscopically.

**Flash Point.** The lowest temperature at which vapors from a volatile liquid will ignite momentarily upon the application of a small flame under specified conditions; test conditions can be either open or closed-cup.

**Flash Process.** Liquid-vapor system in which the composition remains constant, but the proportion of gas and liquid phases changes as pressure or temperature change.

**Flash Separation.** Process for separation of gas (vapor) from liquid components under reduced pressure; the liquid and gas remain in contact as the gas evolves from the liquid.

**Flash Spectroscopy.** The study of the electronic stages of molecules after they absorb energy from an intense, brief light flash.

**F Line.** A green-blue line in the spectrum of hydrogen, at a wavelength of 486.133 nanometers.

**Floc Point** The temperature at which wax or solids separate from kerosine and other illuminating oils as a definite floc.

**Floc Test** A quantitative test applied to kerosine and other illuminating oils to detect substances rendered insoluble by heat.

**Flood's Equation.** A relation used to determine the liquidus temperature in a binary fused salt system.

**Fluorescein** (resorcinolphthalein; diresorcinolphthalein; see also uranine)  $C_{20}H_{12}O_6$ . C.I. 45350.

Properties: Orange-red, crystalline powder; very dilute alkaline solutions exhibit intense, greenish-yellow fluorescence by reflected light, while the solution is reddish-orange by transmitted light; m.p., decomposes at  $290^{\circ}\text{C}$ ; soluble in dilute alkalis, boiling alcohol, ether and dilute acids, glacial acetic acid; insoluble in water, benzene, chloroform. Combustible; low toxicity.

**Derivation:** By heating phthalic anhydride and resorcinol.

**Grades:** The sodium salt (uranine) and potassium salt are marketed.

**Uses:** Dyeing sea water for spotting purposes; tracer to locate impurities in wells; dyeing silk and wool; diagnostic aid in ophthalmology; indicator and reagent for bromine.

### Fluorescence

1. Emission of electromagnetic radiation that is caused by the flow of some form of energy into the emitting body and which ceases abruptly when the excitation ceases.
2. Emission of electromagnetic radiation that is caused by the flow of some form of energy into the emitting body and whose decay, when the excitation ceases, is temperature-independent.
3. Gamma radiation scattered by nuclei which are excited to and radiate from an excited state.

**Fluorescence Indicator** An indicator\* which alters the intensity of, or colour of, its fluorescence according to *e.g.* the pH or redox potential of the solution. Used in the titration of deeply coloured or turbid solutions (*e.g.* wine or fruit juices) *e.g.* acridine changes its fluorescence from green to violet in the pH range 4.8-5.0.

**Fluorescence Spectra** Emission spectra of fluorescence in which an atom or molecule is excited by absorbing light and then emits light of characteristic frequencies.

**Fluorescent Dye** A highly reflective dye that serves to intensify color and add to the brilliance of a fabric.

**Fluorescent Pigment** A pigment capable of absorbing both visible and nonvisible electromagnetic radiations and releasing them quickly as energy of desired wavelength; examples are zinc sulfide or cadmium sulfide.

**Fluorometric Analysis.** A method of chemical analysis in which a sample, exposed to radiation of one wavelength, absorbs this radiation and reemits radiation of the same or longer wavelength in about  $10^{-9}$  second; the intensity of reemitted radiation is almost directly proportional to the concentration of the fluorescing material. Also known as fluorescence analysis fluorometry.

**fluorometry.** See fluorometric analysis.

**Folin solution.** An aqueous solution of 500 grams of ammonium sulfate, 5 grams of uranium acetate, and 6 grams of acetic acid in a volume of 1 liter; used to test for uric acid.

**Forbidden Line.** A spectral line associated with a transition forbidden by selection rules; optically this might be a magnetic dipole or electric quadrupole transition.

**Force Constant.** An expression for the force acting to restrain the relative displacement of the nuclei in a molecule.

**Forensic Chemistry.** The application of chemistry to the study of materials or problems in cases where the findings may be presented as technical evidence in a court of law.

**Formal Charge.** The apparent charge of an element in a compound for example, magnesium has a formal charge of  $+2$  in  $MgO$  and oxygen has a charge of  $-2$ .

**Formation Factor.** The ratio between the conductivity of an electrolyte and that of a rock saturated with the same electrolyte. Also known as resistivity factor.

## Formula

1. A combination of chemical symbols that expresses a molecule's composition.
2. A reaction formula showing the interrelationship between reactant and products.

**Formula Weight.** The sum of the atomic weights represented in a chemical formula. Thus, since the atomic weight of hydrogen is 1, and oxygen is 16, the formula weight of water ( $H_2O$ ) is 18, (Approximate atomic weights used).

**Foulger's Test.** A test for fructose in which urea, sulfuric acid, and stannous chloride are added to the solution to be tested, the solution is boiled, and in the presence of fructose a blue coloration forms.

**Four-degree Calorie.** The heat needed to change the temperature of 1 gram of water from 3.5 to 4.5°C.

**Fraas Breaking Point.** The temperature at which a solid bitumen becomes brittle when a thin film on a metal plate is flexed under standard conditions.

**Fractional Condensation.** Separation of components of vaporized liquid mixtures by condensing the vapors in stages (partial condensation); highest-boiling-point components condense in the first condenser stage, allowing the remainder of the vapor to pass on to subsequent condenser stages.

**Fractional Crystallization.** The process of separating the components of a mixture containing two or more materials by making use of the change in solubility with temperature. Fractional crystallization is only possible when the solubility and phase relationships of the material are suitable. It is also possible to effect separation of materials when the rates of crystallization differ sufficiently to enable one component to be precipitated leaving the other in a state of supersaturation.

**Fractional Distillation.** A method to separate a mixture of several volatile components of different boiling points; the mixture is distilled at the lowest boiling point, and the distillate is collected as one fraction until the temperature of the vapor rises, showing that the next higher boiling component of the mixture is beginning to distill; this component is then collected as a separate fraction.

**Fractional Precipitation.** Method for separating elements or compounds with similar solubilities by a series of analytical precipitations, each one improving the purity of the desired element.

**Fractionating Column.** An apparatus used widely for separation of fluid (gaseous or liquid) components by vapor-liquid fractionation or liquid-liquid extraction or liquid-solid adsorption.

**Fractionation** Separation of a mixture in successive stages, each stage removing from the mixture some proportion of one of the substance, as by differential solubility in water-solvent mixtures.

**Franck-condon Principle.** The principle that in any molecular system the transition from one energy state to another is so rapid that the nuclei of the atoms involved can be considered to be stationary during the transition.

**Fraude's Reagent.** See perchloric acid.

**Fraunhofer.** A unit for measurement of the reduced width of a spectrum line such that a spectrum line's reduced width in fraunhofers equals  $10^6$  times its equivalent width divided by its wavelength.

**Fraunhofer Lines.** The dark lines constituting the Fraunhofer spectrum.

**Fraunhofer Spectrum.** The absorption lines in sunlight, due to the cooler outer layers of the sun's atmosphere.

**Frazer-Brace Extraction Method.** A method used to extract oil from citrus fruit; utilizes a machine which has abrasive carborundum rolls to rasp the peel from the fruit under a water spray; the water-and-peel mixture is screened and settled to allow oil separation.

**Freeze-Drying.** Removal of water (or other solvent) from the frozen solid at e.g.  $-40^{\circ}$  to  $10^{\circ}\text{C}$  at low pressure. Costly but avoids damage to sensitive materials; used for biological specimens and some foodstuffs.

**Freezing Mixtures.** A mixture used for small-scale-refrigeration consisting of salt, ice and water which freezes well below  $0^{\circ}\text{C}$ . Dry ice or liquid nitrogen and organic solvents are also used to prepare freezing mixture.

**Freezing Mixture.** A mixture of substances whose freezing point is lower than that of its constituents.

**Freezing Point.** The temperature at which a liquid and a solid may be in equilibrium.

**Freezing-point Depression.** The lowering of the freezing point of a solution compared to the pure solvent; the depression is proportional to the active mass of the solute in a given amount of solvent.

**Friedel's Law.** The law that x-ray or electron diffraction measurements cannot determine whether or not a crystal has a center of symmetry.

**F-sum Rule.** The rule that the sum of the  $f$  values (or oscillator strengths) of absorption transitions of an atom in a given state, minus the sum of the  $f$  values of these emission transitions in that state, equals the number of electrons which take part in these transitions. Also known as Thomas-Reiche-Kuhn sum rule.

**Fume Hood.** A fume-collection device over an enclosed shelf or table, so that experiments involving poisonous or unpleasant fumes or gases may be conducted away from the experimental area.

**Fumes.** Particulate matter consisting of the solid particles generated by condensation from the gaseous state, generally after volatilization from melted substances, and often accompanied by a chemical reaction, such as oxidation.

**Fuming Nitric Acid.** Concentrated nitric acid containing dissolved nitrogen dioxide; may be prepared by adding formaldehyde to concentrated nitric acid.

**Fuming Sulfuric Acid.** Concentrated sulfuric acid containing dissolved sulfur trioxide. Also known as oleum.

**Functional Group.** An atom or group of atoms, of acting as a unit, that has replaced a hydrogen atom in a hydrocarbon molecule

and whose presence imparts characteristic properties to this molecule; frequently represented as R—.

**Fundamental Series** A series occurring in the line spectra of many atoms and ions having one, two or three electrons in the outer shell, in which the total orbital angular momentum quantum number changes from 3 to 2.

**Funicular Distribution.** The distribution of a two-phase, immiscible liquid mixture (such as oil and water, one a wetting phase, the other nonwetting) in a porous system when the wetting phase continuous over the surface of the solids.

**Furfural Extraction.** Process for the refining of lubricating oils and other organic materials by contact with furfural.

**Fused-salt Electrolysis.** Electrolysis with use of purified fused salts as raw material and as an electrolyte.

**Fusion Tube.** Device used for the analysis of the elements in a compound by fusing them with another compound for example, analysis of nitrogen in organic compounds by fusing the compound with sodium and analyzing for sodium cyanide.

## G

**Galvanic Series.** The relative hierarchy of metals arranged in order from magnesium (least noble) at the anodic, corroded end through platinum (most noble) at the cathodic, protected end.

**Gamma Emission.** A quantum transition between two energy levels of a nucleus in which a gamma ray is emitted. Also known as gamma decay.

**Gamma Flux Density.** The number of gamma rays passing through a unit area in a unit time.

**Gamma Ray.** A high-energy photon, especially as emitted by a nucleus in a transition between two energy levels.

**Gamma Ray Spectroscopy.** An analytical technique involving the use of gamma radiation, which is emitted from radioactive nuclei in discrete energies. The spectrum of energies and the relative intensities of the gamma rays often characterize the radio-nuclide that emits them; it is these that are determined by gamma ray spectroscopy. It is possible to identify quantitatively the elements present by their characteristic gamma ray spectra as well as to determine radioactive decay rates.

**Gamow-condon-Gurney Theory.** An early quantum-mechanical theory of alpha-particle decay according to which the alpha particle penetrates a potential barrier near the surface of the nucleus by a tunneling properties.

**Gamow-teller Selection Rules.** Selection rule for beta decay caused by the Gamow-Teller interaction; that is, in an allowed transition there is no parity change of the nuclear state, and the spin of the nucleus can either remain unchanged or change by  $=1$ ; transitions from spin 0 to spin 0 are excluded, however.

**Gas Absorption Operation.** The recovery of solute gases present in gaseous mixtures of non-condensables; this recovery is generally achieved by contacting the gas stream with a liquid that offers specific or selective solubility for the solute gas to be recovered, or with an adsorbent (for example, synthetic or natural zeolite) that aspects only specific molecule sizes or shapes.

**Gas Adsorption.** The concentration of a gas upon the surface of a solid substance by attractive forces between the surface and the gas molecules.

**Gas Analysis.** A mixture of gases may be analysed by e.g. :

- (1) Absorbing each constituent preferentially by means of a reagent, e.g.  $\text{CO}_2$  in KOH solution, CO in acid or alkaline CuCl.



- (2) Exploding or burning the gas with oxygen or air and measuring both the change in volume and amount of waste gases formed by absorption.
- (3) Titration as in volumetric analysis, *e.g.*  $\text{NH}_3$  and  $\text{H}_2\text{S}$ .
- (4) Absorbing the gas on a substance which can be weighted both before and after absorption.
- (5) Changes in thermal conductivity, *e.g.* carbon dioxide in flue gas.
- (6) Measurement of i.r. or u.v. spectra.
- (7) Vapor phase chromatography.
- (8) Measurement of magnetic susceptibility.

**Gas-cell Frequency Standard.** An atomic frequency standard in which the frequency-determining element is a gas cell containing rubidium, cesium, or sodium vapor.

**Gas Chromatograph.** The instrument used in gas chromatography to detect volatile compounds present; also used to determine certain physical properties such as distribution or partition coefficients and adsorption isotherms, and as a preparative technique for isolation pure components of certain fractions from complex mixtures.

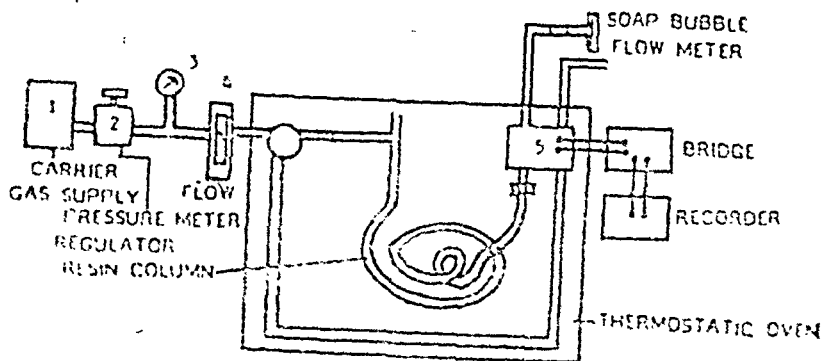
**Gas Chromatography.** Gas chromatography is a separation technique in which the components of a vaporised sample is separate due to the difference in partition coefficient between the mobile gas phase and the stationary phase. In gas chromatography the mobile phase is a gas and the stationary phase is a solid, or a liquid supported on an inert solid. If the stationary phase is a solid, then it is called Gas-solid chromatography (GSC) and if it is a liquid then it is called Gas-liquid chromatography (GLC).

In GLC the sample is introduced in the vapour form at the head of the column containing a liquid stationary phase. The

components of the sample having finite solubility with the stationary liquid phase distribute themselves between the liquid phase and the gas phase according to equilibrium law. The components of the sample are separated from the column by the process of elution. Elution is done by forcing an inert carrier gas like He, or  $N_2$ , through the column. The rates at which the various components move along the column depends upon their tendency to dissolve in the stationary liquid phase. A component which dissolves more in the liquid stationary phase moves slowly, whereas the one which is not soluble moves fast through the column causing the separation of the components.

GLC involves the following parts :

- (1) Carrier gas supply.
- (2) Sample injection system.
- (3) Liquid Column supported on a solid surface, acting as a stationary phase.
- (4) Thermostat.
- (5) Detectors.



- (1) Carrier Gas supply : Chemically inert carrier gases like He, Ne, Ar,  $N_2$  and  $H_2$  can be used of which helium is most widely used. The flow rate of the gas is controlled by pressure regulator.

- (2) Sample injection system : Column efficiency increases when the sample is introduced as vapour and of suitable quantity. The liquid sample is introduced through a micro syringe through a rubber diaphragm into a heated sample port which is at a temperature  $50^{\circ}$  higher than the boiling point of the substance. For ordinary analytical columns the  $10\ \mu\text{l}$  will be used. For capillary columns  $10^{-3}\ \mu\text{l}$  is sufficient.
- (3) Columns : Two types of columns are used in GLC. One type consists of capillary tubing of 0.3-0.5 mm inner diameter, the bore of which is coated with a very thin film of  $\sim 1\ \mu\text{m}$  of the liquid phase. Capillary columns can be of 10m-100m or more in length. The capacity of a capillary can be increased by coating with a porous material such as graphite, a metal oxide or a silicate such that the added surface area increases the amount of liquid retained by the tube and thus the capacity increases.

Packed columns are made of glass or metal tubes of 1-8 mm inside diameter which are designed to hold solid packings. The tubes are ordinary folded or coiled so that they are inserted in a thermostat conveniently.

Solid support for packed columns : The ideal solid support is of spherical particles with a surface area of  $1\ \text{m}^2/\text{g}$ . It should be easily wetted by liquid phase and inert at elevated temperatures. (e.g) Firebrick. Kieselghur.

Liquid Phase : The conditions fulfilled by the liquid phase are :

- (1) Low volatility : The boiling point of the liquid must be at least  $200^{\circ}\text{C}$  higher than the maximum operating temperature for the column.
- (2) Thermal stability.
- (3) Chemical inertness.

Column Preparation : The support material is selected according to the required particle size and it is made into a

slurry in a volatile solvent that contains an amount of liquid stationary phase to produce a thin coating of all the particles and it is filled into a glass or stainless fabricated column with gentle tapping or shaking to provide a uniform column. Then the column is fitted into a thermostatic oven for heating. The optimum temperature required depends upon the boiling point of the sample and the degree of separation required. Roughly, a temperature equal to or slightly above the boiling point of the sample results in an elution period of reasonable time.

**Detectors :** There are three detectors in GLC system.

- (1) Thermal conductivity detector,
- (2) Flame ionisation detector,
- (3) Electron capture detector.

- (1) In thermal conductivity detector, the sensing element is an electrically heated source whose temperature at constant electrical power depends on the thermal conductivity of the gas sample. The heated element may be of Pt, W wire or a semiconducting thermistor. In chromatographic applications a double detector is always used. One for sample and one for carrier gas. The resistances of twin detectors are usually compared by incorporating them into a Wheatstone bridge circuit.
- (2) In Flame ionisation detector, the ionic current produced by the ionisation of substances by air/hydrogen flame is measured by an ammeter. Although organic compounds are poorly ionisable, the number of ions produced is equal to number of reduced carbon atoms in the flame. This detector is most popular and sensitive one but more complicated and more expensive than thermal conductivity detectors. It has higher sensitivity but of course destructive of sample.
- (3) In Electron capture detector, the effluent from the column is passed over a  $\beta$  emitter such as Nickel-63 or tritium. An electron from the emitter causes ionisation of the gases. In the absence of organic species, a constant current is passed

between a pair of electrodes results from this ionisation process. The current decreases, however in the presence of organic molecules. This detector is highly sensitive towards electronegative groups such as halogens, peroxides etc.

The applications of GLC are :

- (1) Gas liquid chromatography provides method for separating complex mixtures.
- (2) Retention time and retention volume provide as a means for qualitative identification, while the peak areas give quantitative identification.
- (3) In programmed-temperature chromatography, the column temperature is increased as elution proceeds. Such a procedure has many of the advantages of gradient elution in liquid chromatography. It is used to simplify, improve and accelerate separations. It is particularly useful in the separation and determination of a mixture of normal paraffins.
- (4) Coupling of Gas chromatography to Mass spectroscopy and IR spectroscopy will provide useful information. Instruments of this type make possible identification of hundreds of components that may be present in natural and biological systems. For example, the interfacing of chromatography with spectroscopy has permitted characterisation of odour and flavour components of foods, identification of pollutants, medical diagnosis based on breath components and studies of drug metabolites.

**Gas Chromatography Mass Spectroscopy, GCMS.** Gas chromatography with direct injection of the separated components into a mass spectrometer.

**Gas Cleaning.** The removal of suspended liquid or solid particles from a gas stream with the object of purification.

**Gas-condensate Liquid.** A hydrocarbon, such as propane, butane, and pentane, obtained as condensate when wet natural gas is compressed or refrigerated.

**Gas Dehydrator.** A device or system to remove moisture vapor from a gas stream, usually incorporates desiccant-type packed towers.

**Gas Filter.** A device used to remove liquid or solid particles from a flowing gas stream.

**Gas Generator**

1. A device used to generate gases in the laboratory.
2. A chemical plant for producing gas from coal, for example, water gas.

**Gas-liquid Chromatography.** A form a gas chromatography in which the fixed phase (column packing) is a liquid solvent distributed on an inert solid support. Abbreviated GLC. Also known as gas liquid partition chromatography.

**Gasometric Method.** An analytical technique for gases; the gas may be measured by instrumental methods or through chemical reactions with specific reagents.

**Gas-solid Chromatography.** A form of gas chromatography in which the moving phase is a gas and the stationary phase is a surface-active sorbent (charcoal, silica gel, or activated alumina). Abbreviated GSC.

**Gel Electrophoresis.** Electrophoresis performed in silica gel, a porous, inert medium.

**Gel Filtration.** A type of column chromatography which separates molecules on the basis of size; higher-molecular-weight substances pass through the column first. Also known as molecular exclusion chromatography; molecular sieve chromatography.

**Gel Permeation Chromatography.** Analysis by chromatography in which the stationary phase consists of beads of porous polymeric material such as a cross-linked dextran carbohydrate

derivative sold under the trade name Sephadex; the moving phase is a liquid.

**Geochemical Balance.** The proportional distribution, and the migration rate, in the global fractionation of elements, minerals, or compounds; for example, the distribution of quartz in igneous rocks, its liberation by weathering, and its redistribution into sediments and, in solution, into lakes, rivers, and oceans.

**Geochemical Cycle.** During geologic changes, the sequence of stages in the migration of elements between the lithosphere, hydrosphere, and atmosphere.

**Geochemistry.** The study of the chemical composition of the earth in terms of the physicochemical and geological processes and principles that produce and modify minerals and rocks. Of practical importance in discovering the establishing the limits of ore deposits, petroleum, tar sands, salt, sulfur, and other valuable resources.

**Gibbs Adsorption Equation.** A formula for a system involving a solvent and a solute, according to which there is an excess surface concentration of solute if the solute decreases the surface tension, and a deficient surface concentration of solute if the solute increases the surface tension.

**Gibbs Adsorption Isotherm.** An equation for the surface pressure of surface monolayers,

$$\phi = RT \int_0^p [d(\ln p)]$$

**Giemsa Stain.** A stain for hemopoietic tissue and hemoprotozoa consisting of a stock glycerol methanol solution of eosinates of Azure B and methylene blue with some excess of the basic dyes.

**Gillespie Equilibrium Still.** A recirculating equilibrium distillation apparatus used to establish azeotropic properties of liquid mixtures.

**Girard's Reagent.** "P." Carboxymethylpyridinium chloride hydrazide; acethydrazidepyridinium chloride.



"T." Carboxymethyltrimethyl ammonium chloride hydrazide; trimethylacethydrazide ammonium chloride.  $(\text{CH}_3)_3\text{NCICH}_2\text{CONHNH}_2$ .

Properties : White to faintly pinkish crystals with little or no odor; m.p. 190—200°C; soluble in water; insoluble in oils. "T" is hygroscopic.

Uses : Separation of aldehydes and ketones from natural oily or fatty materials; extraction of hormones.

**Glass Electrode.** An electrode or half cell in which potential measurements are made through a glass membrane, which acts as a cation-exchange membrane; thus, the potential arises from phase boundary and diffusion potentials which, depending on the composition of the glass, are logarithmic functions of the activity of the cations such as  $\text{H}^+$ ,  $\text{Na}^+$ , or  $\text{K}^+$  of the solutions in which the electrode is immersed.

**Glucoside.** One of a group of compounds containing the cyclic forms of glucose, in which the hydrogen of the hemiacetal hydroxyl has been replaced by an alkyl or aryl group.

**Glycoside.** One of a group of organic compounds, of abundant occurrence in plants, which can be resolved by hydrolysis into sugars and other organic substances, known as aglycones. Specifically glycosides are acetals which are derived from a combination of various hydroxy compounds with various sugars. They are designated individually as glucosides, mannosides, galactosides, etc. Glycosides were formerly called glucosides, but the latter term now refers to any glycoside having glucose as its sugar constituent.

**Gold Number.** A measure of the amount of protective colloid which must be added to a standard red gold sol mixed with sodium chloride solution to prevent the solution from causing the sol to coagulate, as manifested by a change in colour from red to blue.



**Gold, Standard.** Pure gold is too soft for use as ornaments or for coinage, and is alloyed with copper or silver, or both. The fineness is expressed either in parts per thousand, or in carats. Pure gold is 24 carat fine, and the five standard alloys of 22, 18, 15, 12 and 9, i.e. parts of gold in 24 of alloy, are legalized. The presence of small quantities of Bi or Pb renders the metal brittle.

**Gooch Crucible.** A ceramic crucible with a perforated base; in analysis it is used for filtration through asbestos or glass.

**Gouy.** An electrokinetic unit equal to the product of the electrokinetic potential and the electric displacement divided by  $4\pi$  times the polarization of the electrolyte.

**Gouy Balance.** Device for measurement of diamagnetic and paramagnetic susceptibilities of samples (solid liquid, solution).

**Grade.** Any of a number of purity standards for chemicals and chemical products established by various specifications.

**Gradient Elution Analysis.** A form of gas-liquid chromatography in which the eluting solvent is changed with time, either by gradually mixing a second solvent of greater eluting power with the first, less powerful solvent, or by a gradual change in pH or other property.

**Gram-atomic Weight.** The atomic weight of an element expressed in grams, that is, the atomic weight on a scale on which the atomic weight of carbon-12 isotope is taken as 12 exactly.

**Gram-equivalent Weight.** The equivalent weight of an element or compound expressed in grams on a scale in which carbon-12 has an equivalent weight of 3 grams in those compounds in which its formal valence is 4.

**Gram-molecular Volume.** The volume occupied by a gram-molecular weight of a chemical in the gaseous state at  $0^{\circ}\text{C}$  and 760 millimeters of pressure (101,325 newtons per square meter).

**Gram Molecular Weight.** The molecular weight of a compound in grams, i.e., the gram molecular weight of carbon dioxide is 44.01 grams.

**Gram-positive, Negative.** A characteristic property of bacteria in reacting to a staining method developed by Gram about 1880. The bacteria are stained with crystal violet, treated with Gram's solution, and again stained with safranine. If the dye is retained the bacteria are called Gram-positive; and vice versa.

**Grassmann's Laws.** Seven laws of colour identification and mixing that form the basis of modern analytical colorimetry.

**Grass-roots Plant.** A complete plant erected on a virgin site.

**Grating.** See diffraction grating.

**Grating Constant.** The distance between consecutive grooves of a diffraction grating.

**Grating Spectrograph.** A grating spectroscope provided with a photographic camera or other device for recording the spectrum.

**Grating Spectroscope.** A spectroscope which employs a transmission or reflection grating to disperse light, and usually also has a slit, a mirror or lenses to collimate the light sent through the slit and to focus the light dispersed by the grating into spectrum lines, and an eyepiece for viewing the spectrum.

**Gravimetric Absorption Method.** A method of measuring the moisture content of a gas in which a known volume of gas is passed through a suitable desiccant, such as phosphorus pentoxide or silica gel, and the change in weight of the desiccant is observed.

**Gravimetric Analysis.** That branch of quantitative analytical chemistry in which a desired constituent is converted, usually by precipitation or combustion, to a pure compound or element, of definite known composition, and is weighed; in a few cases a compound or element is formed which does not contain the constituent but bears a definite mathematical relationship to it.

**Gravity Cell.** An electrolytic cell in which two ionic solutions are separated by means of gravity.

**Gray-king Assay.** An assay test for coal giving the percentages of gas, tar, liquor and coke obtained in a small-scale carbonization

at 600° or 900°C. The appearance of the coke residue is a measure of the coking properties of the coal and this is used as one of the parameters of the National Coal Board Classification of coals.

**Grid Spectrometer.** A grating spectrometer in which a large increase in light flux without loss of resolution is achieved by replacing entrance and exit slits with grids consisting of opaque and transparent areas, patterned to have large transmittance only when the entrance grid image coincides with that of the exist grid.

**Griess Reagent.** A reagent used to test for nitrous acid; it is a solution of sulfanilic acid,  $\alpha$ -naphthylamine and acetic acid in water.

**Grignard Reagent.** RMgX The organometallic halide formed in the Grignard reaction; an example is  $C_2H_5MgCl$ ; it is useful in organic synthesis.

**Grignard Synthesis.** Use of the Grignard reagent in any one of a vast number of reactions, usually condensations; typical syntheses involve formation of a hydrocarbon, acid, ketone, or secondary or tertiary alcohol.

**Gum Test.** A standard ASTM test to determine the amount of gums in gasolines.

**Gunbarrel.** An atmospheric vessel used for treatment of waterflood waste water.

**Gunzberg Reagent.** A solution of 2 grams of vanillin and 4 grams of phloroglucinol in 80 milliliters of 95% alcohol; used as a test reagent for determining free hydrochloric acid in gastric juice.

**Gurney-mott Theory.** A theory of the photographic process that proposes a two-stage mechanism; in the first stage a light quantum is absorbed at a point within the silver halide gelatin, releasing a mobile electron and a positive hole; these mobile

defects diffuse to trapping sites (sensitivity centers) within the volume or on the surface of the grain; in the second stage, trapped (negatively charged) electron is neutralized by an interstitial (positively charged) silver ion, which combines with the electron to form a silver atom; the silver atom is capable of trapping a second electron, after which the process repeats itself, causing the silver speck to grow.

**Gutzeit Test.** A test for arsenic; zinc and dilute sulfuric acid are added to the substance, which is then covered with a filter paper moistened with mercuric chloride solution; a yellow spot forms on the paper if arsenic is in the sample.

## H

**Half-Cell Potential.** In electrochemical cells, the electrical potential developed by the overall cell reaction; can be considered, for calculation purposes, as the sum of the potential developed at the anode and the potential developed at the cathode, each being a half-cell.

**Haloform Reaction.** Halogenation of acetaldehyde or a methyl ketone in aqueous basic solution; the reaction is characteristic of compounds containing a  $\text{CH}_3\text{CO}$  group linked to a hydrogen or to another carbon.

**Hammett Acidity Function.** An expression for the acidity of a medium, defined as  $h_0 = K_{\text{BH}^+} [\text{BH}^+]/[\text{B}]$ , where  $K_{\text{BH}^+}$  is the dissociation constant of the acid form of the indicator, and  $[\text{BH}^+]$  and  $[\text{B}]$  are the concentrations of the protonated base and the unprotonated base respectively.

**Hanus Solution.** Iodine monobromide in glacial acetic acid; used to determine iodine values in oils containing unsaturated organic compounds.

**Hardness.** The amount of calcium carbonate dissolved in water, usually expressed as part of calcium carbonate per million parts of water.

**Hardness Test.** Test to determine the calcium and magnesium content of water.

**Hard Water.** Water that contains certain salts, such as those of calcium or magnesium, which form insoluble deposits in boilers and form precipitates with soap.

**Hardy-schulz Rule.** An increase in the charge of ions results in a large increase in their flocculating power.

**Haring Cell.** An electrolytic cell with four electrodes used to measure electrolyte resistance and polarization of electrodes.

**Harmonic Vibration-rotation Band.** A vibration-rotation band of a molecule in which the harmonic oscillator approximation holds for the vibrational levels, so that the vibrational are equally spaced.

**Hartmann Diaphragm.** Comparison device for positive-element-identification readings from emission spectra.

**Hartmann Test.** A test for spectrometers in which light is passed through different parts of the entrance slit; any resulting changes of the spectrum indicate a fault in the instrument.

**Hartree.** A unit of energy used in studies of atomic spectra and structure, equal (in centimeter-gram-second units) to  $4\pi^2 me^4/h^2$ , where  $e$  and  $m$  are the charge and mass of the electron, and  $h$  is Planck's constant; equal to approximately 27.21 electronvolts or  $4.360 \times 10^{-18}$  joule.

**Hartree Units.** A system of units in which the unit of angular momentum is Planck's constant divided by  $2\pi$ , the unit of mass is the mass of the electron, and the unit of charge is the charge of the electron. Also known as atomic units.

**Hauy Law.** The law that for a given crystal there is a set of ratios such that the ratios of the intercepts of any crystal plane on the crystal axes are rational fractions of these ratios.

**Heat of Activation.** The increase in enthalpy when a substance is transformed from a less active to a more reactive form at constant pressure.

**Heat of Association.** Increase in enthalpy accompanying the formation of 1 mole of a coordination compound from its constituent molecules or other particles at constant pressure.

**Heat of Combustion.** The amount of heat released in the oxidation of 1 mole of a substance at constant pressure, or constant volume. Also known as heat value; heating value.

**Heat of Decomposition.** The change in enthalpy accompanying the decomposition of 1 mole of a compound into its elements at constant pressure.

#### **Heat of Dilution**

1. The increase in enthalpy accompanying the addition of a specified amount of solvent to a solution of constant pressure. Also known as integral heat of dilution; total heat of dilution.
2. The increase in enthalpy when an infinitesimal amount of solvent is added to a solution at constant pressure. Also known as differential heat of dilution.

**Heat of Dissociation.** The increase in enthalpy at constant pressure, when molecules break apart or valence linkages rupture.

**Heat of Formation.** The increase in enthalpy resulting from the formation of 1 mole of a substance from its elements of constant pressure.

**Heat of Hydration.** The increase in enthalpy accompanying the formation of 1 mole of a hydrate from the anhydrous form of the compound and from water at constant pressure.

**Heat of Ionization.** The increase in enthalpy when 1 mole of a substance is completely ionized at constant pressure.

**Heat of Linkage.** The bond energy of a particular type of valence linkage between atoms in a molecule, as determined by the energy required to dissociate all bonds of the type in .1 mole of the compound divided by the number of such bonds on a compound.

### **Heat of Reaction**

1. The negative of the change in enthalpy accompanying a chemical reaction at constant pressure.
2. The negative of the change in internal energy accompanying a chemical reaction at constant volume.

**Heat of Solution.** The enthalpy of a solution minus the sum of the enthalpies of its components. Also known as integral heat of solution; total heat of solution.

**Heavy.** A nontechnical word used in a number of scientific senses :

1. referring to atomic weight (heavy water, heavy metal);
2. referring to production volume (heavy chemical);
3. referring to physical weight (heavy spar);
5. referring to thickness (heavy-gauge wire); referring to distillation range (heavy oil).

**Heavy Chemical.** A chemical produced in tonnage quantities, often in a relatively impure state. Examples are sodium chloride, sulfuric acid, soda ash, salt cake, sodium hydroxide, etc.

**HEDTA.** See hydroxyethylethylenediaminetriacetic acid.

**Hebner Number.** The percent by weight of water-insoluble fatty acids in oils and fats.

**Helium Spectrometer.** A small mass spectrometer used to detect the presence of helium in a vacuum system; for leak detection, a jet of helium is applied to suspected leaks in the outer surface of the system.

**Henderson Equation for pH.** An equation for the pH of an acid during its neutralization:  $\text{pH} = \text{pK}_a + \log [\text{salt}]/[\text{acid}]$  where  $\text{pK}_a$  is the logarithm to base 10 of the reciprocal of the

dissociation constant of the acid; the equation is found to be useful for the pH range 4–10, providing the solutions are not too dilute.

**Hengstebeck Approximation.** A method of calculation to estimate the distribution of non-key components in distillation column products.

**Henry's Law.** The law that at sufficiently high dilution in a liquid solution, the fugacity of a nondissociating solute becomes proportional to its concentration.

**Hess's Law.** The law that the evolved or absorbed heat in a chemical reaction is the same whether the reaction takes one step or several steps. Also known as the law of constant heat summation.

**Heteroazeotrope.** Liquid mixture that is not completely miscible in all proportions in the liquid phase, yet does not form an azeotrope. Also known as heterogeneous zeotrope.

**Heterotopic Ligands.** Constitutionally identical ligands whose separate replacement by a different ligand gives rise to isomeric structures.

**Heterotropic Effect.** The interaction between different ligands, such as the effect of an inhibitor or activator on the binding of a substrate by an enzyme.

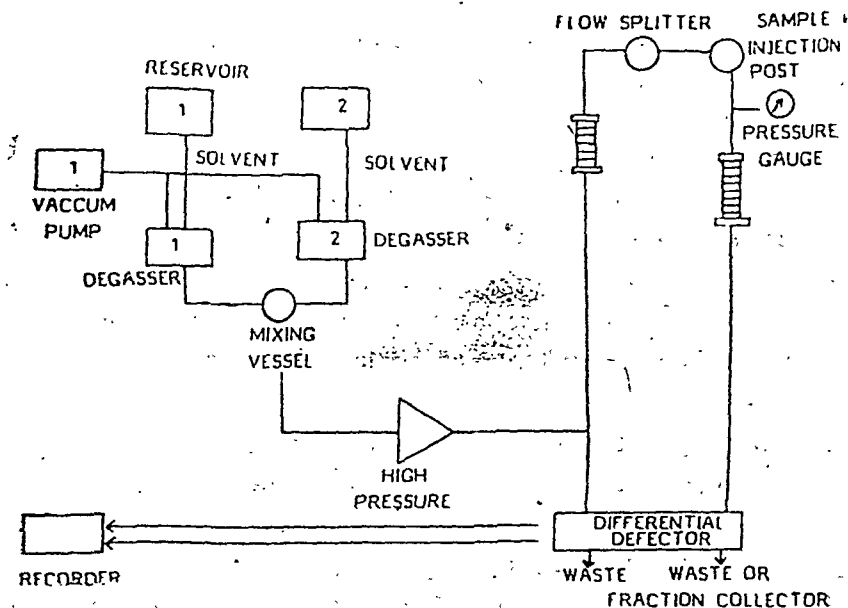
**Hexachloroethane  $\text{Cl}_3\text{CCl}_3$ .** Colorless crystals with a camphorlike odor, melting point  $185^\circ\text{C}$ , toxic; used in organic synthesis, as a retarding agent in fermentation, and as a rubber accelerator. Also known as carbon trichloride; perchloroethane.

**Higbie Model.** Mass-transfer theory for packed absorption towers, stating that liquid flows across each packing piece in laminar flow and is mixed with other liquids melting it at the points of discontinuity between packing elements.

**High-frequency Titration.** A conductimetric titration in which two electrodes are mounted on the outside of the beaker or vessel



containing the solution to be analyzed and an alternating current source in the megahertz range is used to measure the course of a titration.



**High Performance Liquid Chromatography (HPLC).** Gas chromatography even though a most advanced separation technique has its own limitations, especially in the analysis of samples having (a) high boiling point, (b) high molecular weight, (c) sample which are labile. These were overcome by high pressure liquid chromatography which basically is column chromatography working at high pressures, thereby reducing the elution time. Coupled of these are the liquid chromatograph detectors which make estimation both quantitatively and qualitatively possible :

- (1) **Solvent reservoir and degassing system :** A modern HPLC equipment contains glass or stainless steel reservoirs containing solvent. The reservoirs are provided with degassing system to remove the dissolved gases. Degassers may consists of a vacuum pumping system, a distillation system or

a device for heating and stirring the solvent. Separation employed by a single solvent is called as isocratic elution and with mixed solvents is called gradient elution.

- (2) **Pumps :** Most HPLC pumps provide a pressure of 4000—6000 Psi (lbs/m<sup>2</sup>), with a flow delivery rate of 3 ml/min. The flow rate should be constant to  $\pm 2\%$  screwdriver syringe type, or reciprocating pump or pneumatic pumps are used for producing high pressures to the mobile phase which is not hazardous as liquids are less compressible.
- (3) **Precolumns :** Some HPLC instruments are equipped with precolumns which contain packings identical to that in the analytical column. The purpose of the precolumn is to remove the impurities from the solvent, and thus prevent contamination of analytical column, precolumn saturates the mobile phase with the liquid which makes the stationary phase.

In the sample injection system, volume of 2 to 10  $\mu$ l are injected through a syringe. HPLC columns are packed with finely divided silica gel with a pressure of 600 Psi. The typical columns are of 15 to 150 cm length and 2 to 3 mm inside diameter. Packing material can also be alumina or ion-exchange resins.

**Temperature control :** Liquid chromatography is conducted at room temperature without thermostating. Water jacketed columns are also available when precise temperature control is necessary.

**Detector :** HPLC detectors are based on absorption of UV or visible radiation. Infra-red detectors, differential refractive index detectors are also used. Mass spectrometry and flame ionisation detectors are also used for quantitative identification.

**High Polymer.** A large molecule (of molecular weight greater than 10,000) usually composed of repeat units of low-molecular weight species; for example, ethylene or propylene.

**High-pressure Chemistry.** The study of chemical reactions and phenomena that occur at pressures exceeding 10,000 bars (a bar is nearly equivalent to a kilogram per square centimeter), mainly concerned with the properties of the solid state.

**High-vacuum Insulation.** High vacuum between the walls of double-wall vessels to serve as thermal insulation at ultralow (cryogenic) temperatures, such as in Dewar vessels.

**Hinsberg Test.** A test to distinguish between primary and secondary amines; it involves reaction of an amine with benzene disulfonyl chloride in alkaline solution; primary amines give sulfonamides that are soluble in basic solution; secondary amines give insoluble derivatives; tertiary amines do not react with the reagent.

**Hittorf Method.** A procedure for determining transference numbers in which one measures changes in the composition of the solution near the cathode and near the anode of an electrolytic cell, due to passage of a known amount of electricity.

**Hodgson Number.** Method of predicting the metering error during pulsating gas flow when a surge tank is located between the pulsation source (pump or compressor) and the meter (orifice, nozzle, or venturi).

**Hofmann Amine Separation.** A technique to separate a mixture of primary, secondary, and tertiary amines; they are heated with ethyl oxalate; there is no reaction with tertiary amines, primary amines form a diamide, and the secondary amines form a monoamide; when the reaction mixture is distilled, the mixture is separated into components.

**Hofmann Exhaustive Methylation Reaction.** The thermal decomposition of quaternary ammonium hydroxide compounds to yield an olefin and water; an exception is tetramethylammonium hydroxide, which decomposes to give an alcohol.

**Hofmann Mustard-oil Reaction.** Preparation of alkylisothiocyanates by heating together a primary amine, mercuric chloride, and carbon disulfide.

**Hofmann's Violet** (triethylrosaniline hydrochloride)  $C_{26}H_{32}N_3HCl$ . C.I. 42510. Water-soluble green powder. Used as dye for inks and textiles; biological stain.

**Hofmeister Series.** An arrangement of anions or cations in order of decreasing ability to produce coagulation when their salts are added to lyophilic soils. Also known as lyotropic series.

**Hole-burning Spectroscopy.** A method of observing extremely narrow line widths in certain ions and molecules embedded in crystalline solids, in which broadening produced by crystal-site-dependent statistical field variations is overcome by having a monochromatic laser temporarily remove ions or molecules at selected crystal sites from their absorption levels, and observing the resulting dip in the absorption profile with a second laser beam.

**Hopkins cole Reaction.** The appearance of a violet ring when concentrated sulfuric acid is added to a mixture that includes a protein and glyoxylic acid; however, gelatin and zein do not show the reaction.

**Horizontal Chromatography.** Paper chromatography in which the chromatogram is horizontal instead of vertical.

**Hortvet Sublimator.** Device for the determination of the condensation temperature (sublimation point) of sublimed solids.

**Huber's Reagent.** An aqueous solution of ammonium molybdate and potassium ferrocyanide used for detecting free mineral acid. With the exception of boric acid and arsenic trioxide, free mineral acids produce a reddish-brown precipitate, or a turbidity with the reagent.

**Hubl's Reagent**

- (a) 50 grams iodine dissolved in 1 litre of 95% alcohol.
- (b) 60 grams mercuric chloride dissolved in 1 liter of alcohol.
- (c) Make up an iodine monochloride solution from (a) and (b). Add in excess to a known weight of the fat or oil dissolved

in chloroform. The excess of iodine chloride can be estimated by the potassium iodide and thiosulfate method. By running a blank test, the amount of iodide absorbed can be estimated.

Use : Determination of iodine values of oils and fats.

**Hull Cell.** An electrodeposition cell that operates within a simultaneous range of known current densities.

**Humidity Indicator.** A cobalt salt (e.g., cobaltous chloride) that changes color as the humidity of the environment changes. Cobaltous compounds are pink when hydrated and greenish-blue when anhydrous.

**Humidity, Relative.** The percentage relation between the actual amount of water vapor in a given volume of air at a definite temperature and the maximum amount of water vapor that would be present if the air were saturated with water vapor at that temperature.

**Hydrogen Electrode.** A noble metal (such as platinum) or large surface area covered with hydrogen gas in a solution of hydrogen ion saturated with hydrogen gas; metal is used in a foil form and is welded to a wire sealed in the bottom of hollow glass tube, which is partially filled with mercury; used as a standard electrode with a potential of zero to measure hydrogen ion activity.

**Hydrogen Equivalent.** The number of replaceable hydrogen atoms or hydroxyl groups in a molecule of an acid or a base.

**Hydrogen Ion Concentration.** The normality of a solution with respect to hydrogen ions,  $H^+$ ; it is related to acidity measurements in most cases by  $pH = \log 1/2 [1/(H_+)]$ , where  $(H^+)$  is the hydrogen ion concentration in gram equivalents per liter of solution.

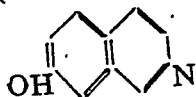
**Hydrogen Ion Exponent.** An expression of pH as  $-\log C_H$ , where  $C_H$  = hydrogen ion concentration.

## Hygroscopic

**Hydrogen Line.** A spectral line emitted by neutral hydrogen having a frequency of 1420 megahertz and a wavelength of 21 centimeters; radiation from this line is used in radio astronomy to study the amount and velocity of hydrogen in the Galaxy.

**Hydrogeochemistry.** The study of the chemical characteristics of ground and surface waters as related to areal and regional geology.

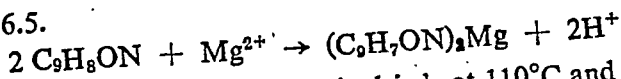
**8-Hydroxy Quinoline. (Oxine):** The structure of the reagent is



The reagent is prepared in alcohol and is useful for the precipitation of  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Al^{3+}$ ,  $Fe^{2+}$ ,  $Bi^{3+}$ ,  $Ga^{3+}$ .

$Al^{3+}$  is separated from  $Be^{2+}$  using buffer solution at a pH of 5.8.

Similarly  $Mg^{2+}$  is separated from its slightly acidic solution at pH 6.5.



The metal oxinate complex is dried at  $110^\circ C$  and weighed. The oxinate can also be dissolved in HCl and can be estimated by volumetric method using suitable oxidising agents like  $KBrO_3$ .

## Hygroscopic

1. Possessing a marked ability to accelerate the condensation of water vapor; applied to condensation nuclei composed of salts which yield aqueous solutions of a very low equilibrium vapor pressure compared with that of pure water at the same temperature.
2. Pertaining to a substance whose physical characteristics are appreciably altered by effects of water vapor.
3. Pertaining to water absorbed by dry soil minerals from the atmosphere; the amounts depend on the physicochemical character of the surfaces, and increase with rising relative humidity.

**Hyperchromicity.** An increase in the absorption of ultraviolet light by polynucleotide solutions due to a loss of the ordered secondary structure.

**Hyperfine Structure.** A splitting of spectral lines due to the spin of the atomic nucleus or to the occurrence of a mixture of isotopes in the element. Abbreviated, hfs.

## I

**Ice Point.** The true freezing point of water; the temperature at which a mixture of air-saturated pure water and pure ice may exist in equilibrium at a pressure of 1 standard atmosphere (101,325 newtons per square meter).

**Ideal Solution.** A solution that conforms to Raoult's law over all ranges of temperature and concentration and shows no internal energy change on mixing and no attractive force between components.

**Ignition Point.** See ignition temperature.

**Ignition Temperature.** The minimum temperature at which a fuel can be ignited. The temperature obtained will depend on the technique used and on the air-fuel ratio of the mixture. A common method is to drop liquid fuel or pass stream or fuel gas into a container containing air or oxygen kept at a known temperature.

**Ilkovic Equation.** The relation between diffusion current,  $i_d$ , and the concentration  $c$  in polarography which in its simplest form is  $i_d = k'c$ .

**Immersion Sampling.** Collection of a liquid sample for laboratory or other analysis by immersing a container in the liquid and filling it.

**Immiscible.** Pertaining to liquids that will not mix with each other.

**Impact Resistance.** A measure (generally approximate) of the capacity of a substance to withstand shock or impact under particular test conditions. Izod and Charpy test are examples of particular tests.

**Impurity.** The presence of one substance in another in such low concentration that it cannot be measured quantitatively by ordinary analytical methods. It is impossible to prepare an ideally pure substance. In certain metal crystal lattices foreign substances can exist in as low a concentration as one millionth of an atomic percent. For example, arsenic atoms are present in germanium crystals in this percentage; this fact is largely responsible for the semiconducting properties of germanium. Here the impurity is beneficial, but often it is detrimental, for example, in graphite used as a moderator in nuclear reactors, and in many metallic catalysts. In the air, trace amounts of sulfur dioxide and carbon monoxide are potentially dangerous impurities in concentrations of 5 ppm of  $\text{SO}_2$  and 50 ppm for CO. See also purity, chemical; trace element; air pollution; semiconductor; purification.

**Inclusion Complex.** Crystalline mixture in which the molecules of one component are contained within the crystal lattice of another component. Also known as inclusion compound.

**Independent Migration Law.** The law that each ion in a conductometric titration contributes a definite amount to the total conductance, irrespective of the nature of the other ions in the electrolyte.

**Indicator.** An organic substance (usually a dye or intermediate) which indicates by a change in its color the presence or absence or concentration of some other substance, or the degree of reaction between two or more other substances. The most common example is the use of acid-base indicators such as litmus, phenolphthalein, and methyl orange to indicate the presence or absence of acids and bases, or the approximate concentration



of hydrogen ion in a solution. Their chief use is in analytical chemistry. The pH ranges of several typical indicators are as follows :

alizarin yellow R	10.1—12.0	yellow to red
methyl orange	3.8—4.4	red to yellow
phenolphthalein	8.3—10.0	colorless to red
phenol red	6.8—8.4	yellow to red
litmus	4.4—8.3	red to blue
Congo red	3.0—5.2	blue to red
bromthymol blue	6.0—7.6	yellow to blue
Chlorphenal red	5.2—6.8	yellow to red
cresol purple	7.4—9.0	yellow to purple

See also titration; pH.

### Indigo

1. A blue dye extracted from species of the *Indigofera* bush.
2. See indigo blue.

**Indigo Blue**  $C_{16}H_{10}O_2N_2$ . A component of the dye indigo, crystallizing as dark-blue rhomboids that break down at 30°C, that are soluble in hot aniline and hot chloroform, and that are also made synthetically; used as a reagent and a dye. Also known as indigo.

**Inductively Coupled Plasma-atomic Emission Spectroscopy.** A type of atomic spectroscopy in which the light emitted by atoms and ions in an inductively coupled plasma is observed. Abbreviated ICP-AES.

**Inert Atmosphere.** A nonreactive gas atmosphere, such as nitrogen, carbon dioxide, or helium; used to blanket reactive liquids in storage, to purge process lines and vessels of reactive gases and liquids, and to cover a reaction mix in a partially filled vessel.

**Infrared.** The region of the electromagnetic spectrum including wave lengths from 0.78 micron to about 300 microns (*i.e.*, longer than visible light and shorter than microwave).

Use : Spectroscopic analysis; medicine; baking of enamels; drying; photography.

**Infra-red Radiation, i.r.** Radiation of frequency less than about  $10^{13}$  per sec ( $10\,000\text{ cm}^{-1}$ ), *i.e.* of wavelengths greater than about

$8000\text{ \AA}$ . It is invisible to the human eye, but possesses considerable penetrating power, and photographic plates may be sensitized towards it, so that it finds application in long-distance photography. Heat seeking devices and devices for night viewing rely on detection of i.r. radiation. Many forms of detector are known. Interatomic vibrations in molecules cause absorption in the i.r. region.

**Infrared Spectrometer.** Device used to identify and measure the concentrations of heteroatomic compounds in gases. In many non-aqueous liquids, and in some solids by arc or spark excitation and subsequent measurement of the electromagnetic emissions in the wavelength range of 7.8 to 300 micrometers.

**Infrared Spectrophotometry.** Spectrophotometry in the infrared region, usually for the purpose of chemical analysis through measurement of absorption spectra associated with rotational and vibrational energy levels of molecules.

**Infrared Spectroscopy.** An analytical technique which may measure either (1) the range of wavelengths in the infrared that are absorbed by a specimen, which characterize its molecular constitution (absorption spectroscopy), or (2) the infrared waves emitted by excited atoms or molecules (emission spectroscopy). Extremely hot bodies (stars) emit spectra in which the atomic composition can be determined by characteristic lines such as the sodium D line in the sun's spectrum. Infrared absorption bands identify molecular components and structures, some of which are :

**Absorption**

band ( $\mu$ )	structure indicated
2.3—3.2	OH and NH groups; $\text{H}_2$
3.2—3.33	aromatics, olefins

3.33—3.55

aliphatics

5.7—6.1

aldehydes, ketones, acids, amides

See also microwave spectroscopy; absorption (2)

**Initial Boiling Point.** According to ASTM petroleum-analysis distillation procedures, the recorded temperature when the first drop of distilled vapor is liquefied and falls from the end of the condenser.

**Insoluble.** Incapable of being dissolved in another material; usually refers to solid-liquid or liquid-liquid systems. Abbreviated insol.

**Insoluble Anode.** An anode that resists dissolution during electrolysis.

**Instrument.** Any of a wide variety of devices used for one of the following purposes :

(1) observation (microscope),

(2) measurement (thermometer, thermocouple, flowmeter, balance);

(3) chemical analysis (spectrometer). See also analytical chemistry; instrumentation.

**Instrumentation.** Collective term for sensing devices used to measure, record, and control chemical process variables such as temperature, pressure, flow rate, thickness, liquid level, pH, etc. Such instruments permit automatic correction of variables on a continuous basis. Increasingly sophisticated developments in automatic control technology have enabled many chemical processes to be carried out with a minimum of personnel, particularly petroleum refining. The ultimate in sophisticated instrumentation is utilized in nuclear reactor control.

**Integral Procedure Decomposition Temperature:** Decomposition temperatures derived from graphical integration of the thermogravimetric analysis of a polymer.

**Intercept.** One of the distances cut off a crystal's reference axis by planes.

(DAC—11)

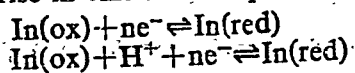
**Interface.** The boundary between any two phases : among the three phases (gas, liquid, and solid), there are five types of interface: gas-liquid, gas-solid, liquid-liquid, liquid-solid, and solid-solid.

**Interface Mixing.** The mixing of two immiscible or partially miscible liquids at the plane of contact (interface).

**Interfacial Angle.** The angle between two crystal faces.

**Interference Spectrum.** A spectrum that results from interference of light, as in a very thin film.

**Internal Indicators.** Internal indicators are organic substances which exhibit different colour in oxidised and reduced states. Normally the indicator should make the sudden change in oxidation potential at the equivalent point. Hence such titrations can be done easily by potentiometric method as it will give a sharp rise in emf at the equivalence point.



According to Nernst equation,

$$\therefore E = E^\circ + \frac{0.0591}{n} \log \left( \frac{\text{In(ox)} \times \text{In}[\text{H}^+]}{\text{In(red)}} \right)$$

When  $\text{In(ox)} = \text{In(red)}$ ,

$$E = E^\circ - \frac{0.0591}{n} \text{pH}$$

Therefore, the observed potential is pH dependent. In order to visualize the colour change, the concentration of one form of the indicator is at least ten times the other/second.

$$\text{Let } \frac{\text{In(ox)}}{\text{In(red)}} = 10$$

$$\therefore E = E^\circ - \frac{0.0591}{n} \text{pH}$$

$$\text{Similarly for } \frac{\text{In(ox)}}{\text{In(red)}} = \frac{1}{10}$$

$$\frac{\text{E(red)}}{\text{Colour}} = E^\circ + \frac{0.0591}{n} \text{pH}$$

Therefore, the colour change depends on the difference of  $\frac{0.0591}{n} \times 2$  where  $n = \text{no. of electron involved in the reaction}$ .

If the indicator concentration is less then the colour change does not depend on the pH value of the solution.

From the titration of Fe(II) salts with ceric sulphate 1, 10 Phenanthroline ion (II) sulphate (ferroin) is the most useful indicator. It has an intense red colour which changes to pale blue colour with strong oxidising agent. 1% solution of diphenyl amine in concentrated  $\text{H}_2\text{SO}_4$  is used for the titration of Fe(II) with  $\text{K}_2\text{Cr}_2\text{O}_7$  solution. At the end point an intense blue violet colour is produced by the indicator. Titration is carried on in the presence of phosphoric acid which lowers the potential of Iron(III)—Iron (II) system so that the potential at the equivalence point is closer to that of the indicator.

**Internal Standard.** The principal line in spectrum analysis by the logarithmic sector method; a quantitative spectroscopy procedure.

**Intracavity Absorption Spectroscopy.** A highly sensitive technique in which an absorbing sample is placed inside the resonator of a broad-band dye laser, and absorption lines are detected as dips in the laser emission spectrum.

**Intrinsic Viscosity.** The ratio of a solution's specific viscosity to the concentration of the solute, extrapolated to zero concentration. Also known as limiting viscosity number.

**Inverse Stark Effect.** The Stark effect as observed with absorption lines, in contrast to emission lines.

**Inverse Zeeman Effect.** A splitting of the absorption lines of atoms or molecules in a static magnetic field; it is the Zeeman effect observed with absorption lines.

**Inversion Spectrum.** Lines in the microwave spectra of certain molecules (such as ammonia) which result from the quantum-mechanical analog of an oscillation of the molecule between two configurations which are mirror images of each other.

**Iodimetry.** The use of iodine in titrations, generally titrated with thiosulphate and converted to I-using starch (blue to colourless)

as indicator. Used indirectly in estimating oxidizing agents which liberate  $I_2$  from acid KI solution.

**Iodine.** A nonmetallic halogen element, symbol I, atomic number 53, atomic weight 196.9044; melts at  $114^\circ C$ , boils at  $184^\circ C$ ; the poisonous, corrosive, dark plates or granules are readily sublimed; insoluble in water, soluble in common solvents; used as germicide and antiseptic, in dyes, tinctures, and pharmaceuticals, in engraving lithography, and as a catalyst and analytical reagent.

**Iodine Monochloride  $ICl$ .**

Properties: Black crystals (alpha and beta forms) or reddish-brown, oily liquid. Soluble in alcohol, water (with decomposition), and dilute hydrochloric acid. M.p. (alpha)  $27^\circ C$ , (beta)  $14^\circ C$ ; b.p.  $101^\circ C$  (dec.) sp. gr. (alpha) 3.18 ( $0^\circ C$ ), (beta), 3.24 (liquid, at  $34^\circ C$ ).

Derivation: By the action of dry chlorine on iodine.

Hazard: Toxic by ingestion and inhalation; strong irritant to eyes and skin.

Uses: Analytical chemistry; organic synthesis.

Shipping regulations: (Rail, Air) Corrosive label. Not acceptable passenger.

**Iodine Number (iodine value).** The percentage of iodine that will be absorbed by a chemically unsaturated substance (vegetable oils, rubber, etc.) in a given time under arbitrary conditions. A measure of unsaturation.

**Iodine Test.** Placing a few drops of potassium iodide solution on a sample to detect the presence of starch; test is positive if sample turns blue.

**Iodine Value.** See iodine number.

**Iodometry.** An application of iodine chemistry to oxidation-reduction titrations for the quantitative analysis in certain chemical compounds, in which iodine is used as a reductant and the

iodine freed in the associated reaction is titrated, usually in neutral or slightly acid mediums with a standard solution of a reductant such as sodium thiosulfate or sodium arsenite, examples of chemicals analyzed are copper(III), gold(VI), arsenic(V), antimony(V), chlorine, and bromine.

**Ion Detector.** Device for detection of presence or concentration of liquid solution ions, such as with a pH meter or by conductimetric techniques.

**Ion Exchange.** When an ionogenic surface is in contact with water or other ionizing solvent an electrical double layer is set up. The counter-ions are partially free and can readily be exchanged for others of the same sign supplied by soluble electrolytes. Thus the sodium in certain silicates can be replaced by potassium by exhaustively washing the material with a solution of HCl (see Base exchange). This is one example of the widespread phenomenon of ion exchange. It is exploited particularly with ion-exchange resins. These are synthetic insoluble cross-linked polymers carrying acidic or basic side-groups. They have high exchange capacity and can be used for many successive reactions. They have many applications, including water-treatment, extraction, separation, analysis and catalysis. Using a 'mixed bed' of anion and cation exchange resins the electrolytes can be removed from a water solution, and very pure water obtained.

**Ion Exchange Capacity.** Ion exchange capacity of resin is defined as the no. of milli-equivalents of ion adsorbed by 1 gm of dry resin. The exchange capacity of anion exchange resin in acid form is determined by treating the resin with Sodium Chloride and the hydrogen ions eluted from the resin column is titrated with a standard solution of alkali of strength N expressed in milli-equivalents per litre.

$$\text{The exchange capacity} = \frac{V \times N}{W}$$

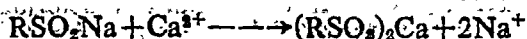
If V ml of alkali of strength N expressed in milli-equivalents per litre required for W gm of resin. Similarly, for

anion exchange resin, the exchange resin capacity is determined by treating the resin with sodium nitrate, and the chloride ion/hydroxide ion eluted is determined by titrating with  $\text{AgNO}_3$  or acid respectively.

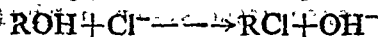
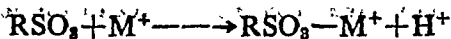
**Ion-exchange Chromatography.** A chromatographic procedure in which the stationary phase consists of ion-exchange resins which may be acidic or basic.

Ion exchange chromatography involves two methods, (1) Batch method (2) Column method.

**Batch method :** Is a single step method in which the resin is made in contact with the solution and on mixing an equilibrium is attained. The extent to which the ions of the solution are exchanged with the resin depends upon the selectivity coefficient. This method will be useful in process like softening of water, and the production of deionised or demineralised water. Softening of water involves an exchange of Calcium and Mg ions from hard water with Sodium ions.



Similarly deionised water is produced by treating the resin with water containing different cations as dissolved salts in which the different cations are exchanged with hydrogen ions or hydroxyl ions of the resin.



The combination of  $\text{H}^+$  and  $\text{OH}^-$  gives almost unionised water which is free from cations. Deionised water finds a large number of commercial applications.

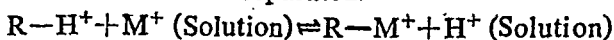
**Column method :** The Column method will be useful for the separation of different ions present in a solution by making use of their differences in adsorption with the resin column. The differences in selectivity coefficient with the resin leads to different migration rates in an ion exchange column.

The column is made of glass fitted with glass wool at the lower end to prevent the flow of resin. Ordinary burette can



also be used as an ion-exchange column. The resin is mixed in water or acid and a slurry is prepared. The slurry is slowly added to the column containing some water. Care should be taken that no air bubbles are formed while packing the resin in the column. The column should never be kept dry and hence always water must be present above the resin column to cause the flow of solution uniformly with the column thus making the separation of different cations according to their selectivity coefficients.

**Ion-exchange Equilibrium.** Ion exchange process involves an exchange of mobile ions from the ion exchanger by ions of similar charge from the solution containing a mixture of cations which are to be separated.



The equilibrium constant of this reaction is represented by

$$K = \frac{a_{RM^+} \cdot a_{H^+}}{a_{RH^+} \cdot a_{M^+}}$$

As activity of solution cannot be determined accurately, the term activity is replaced by concentration term.

$$K_d = \frac{C_{RM^+} \cdot C_{H^+}}{C_{RH^+} \cdot C_{M^+}}$$

Where  $K_d$  is the selectivity coefficient. Large value of selectivity coefficient, greater is the affinity of the ions for the resin.

**Ion Exclusion.** Ion-exchange resin system in which the mobile ions in the resin-gel phase electrically neutralize the immobilized charged functional groups attached to the resin, thus preventing penetration of solvent electrolyte into the resin-gel phase; used in separations where electrolyte is to be excluded from the resin, but not nonpolar materials, as the separation of salt from nonpolar glycerin.

**Ion-exclusion Chromatography.** Chromatography in which the adsorbent material is saturated with the same mobile ions (cationic or anionic) as are present in the sample-carrying eluent (solvent), thus repelling the similar sample ions.

**Ionic Conductance.** The contribution of a given type of ion to the total equivalent conductance in the limit of infinite dilution.

**Ionic Equivalent Conductance.** The contribution made by each ion species of a salt toward an electrolyte's equivconductance.

**Ionic Strength.** A measure of the average electrostatic interactions among ions in an electrolyte; it is equal to one-half the sum of the terms obtained by multiplying the molality of each ion by its valence squared.

**Ion Kinetic Energy Spectrometry.** A spectrometric technique that uses a beam of ions of high kinetic energy passing through a field-free reaction chamber from which ionic products are collected and energy analyzed; it is a generalization of metastable ion studies in which both unimolecular and bimolecular reactions are considered.

**Ion Scattering Spectroscopy.** A spectroscopic technique in which a low-energy (about 1000 electronvolts) beam of inert-gas ions is directed at a surface, and the energies and scattering angles of the scattered ions are used to identify surface atoms. Abbreviated ISS.

**Irradiation.** Exposure to radiation of wavelengths shorter than those of visible light (gamma, x-ray or ultraviolet) either for medical purposes (cancer therapy, removal of skin blemishes), for destruction of bacteria in milk and other foodstuffs, or for inducing polymerization of monomers or vulcanization of rubber. UV irradiation was formerly used to induce activation of vitamin D in milk, and has been used for some time to sterilize the air in operating rooms, etc.

**Irving-Williams Order.** The stabilities of series of complexes with different metals fall into the sequence  $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ . This is known as the Irving-Williams order and is general for many ligands.

**Isoelectric Point.** The pH value of the dispersion medium of a colloidal suspension at which the colloidal particles do not move in an electric field.

**Isoelectric Precipitation.** Precipitation of materials at the isoelectric point (the pH at which the net charge on a molecule in solution is zero); proteins coagulate best at this point.

**Isoelectronic Sequence.** A set of spectra produced by different chemical elements ionized so that their atoms or ions contain the same number of electrons.

**Isohydric.** Referring to a set of solutions with the same hydrogen ion concentration and not affecting the conductivity of each of the various solutions on mixing.

**Isomeric Shift.** Shift in the Mossbauer resonance caused by the effect of the valence of the atom on the interaction of the electron density at the nucleus with the nuclear charge. Also known as chemical shift.

**Isotachophoresis.** A variant of electrophoresis in which ionic species move with equal velocity in the presence of an electric field.

**Isotherm.** Constant temperature line used on climatic maps or in graphs of thermodynamic relations, particularly the graph of pressure-volume relations at constant temperature.

**Isotope-dilution Analysis.** Variation on paper-chromatography analysis; a labeled radioisotope of the same type as the one being quantitated is added to the solution, then quantitatively analyzed afterward via radioactivity measurement.

**Isotope Effect.** The effect of difference of mass between isotopes of the same element on nonnuclear physical and chemical properties, such as the rate of reaction or position of equilibrium, of chemical reactions involving the isotopes.

**Isotope Shift.** A displacement in the spectral lines due to the different isotopes of an element.

**Isotopic Spin.** A quantum-mechanical variable, resembling the angular momentum vector in algebraic structure whose third component distinguished between members of groups of elementary particles, such as the nucleons, which apparently

behave in the same way with respect to strong nuclear forces, but have different charges. Also known as isobaric spin; isospin; i-spin.

**Isotopic Tracer.** An isotope of an element, either radioactive or stable, a small amount of which may be incorporated into a sample material (the carrier) in order to follow the course of that element through a chemical, biological, or physical process, and also follow the larger sample. Also known as isotopic indicator; isotopic label; label; tag.

**Isotropic.** Descriptive of the property of transmitting light equally in all directions; cubic (isometric) crystals have this property, as well as liquids, gases, and most glasses.

**Ivanov Reagent.** A reagent that is similar to a Grignard reagent, and that is formed by reacting an arylacetic acid or its sodium salt with isopropyl magnesium halide.

## J

**J.** A measure of the coupling constant in nuclear magnetic resonance.

**Jacquemart's Reagent.** Analytical reagent used to test for ethyl alcohol; consists of an aqueous solution of mercuric nitrate and nitric acid.

**Jahn-Teller Effect.** The effect whereby, except for linear molecules, degenerate orbital states in molecules are unstable.

**Janecke Coordinates.** Use of a rectangular or Ponchon-type diagram to plot the solvent content of liquid-liquid equilibrium phases; used for solvent-extraction design calculations.

solution, and on distillation anhydrous alcohol leaves the bottom of the column.

**Kikuchi Lines.** A pattern consisting of pairs of white and dark parallel lines, obtained when an electron beam is scattered (diffracted) by a crystalline solid; the pattern gives information on the structure of the crystal.

**Kilo.** Prefix meaning  $10^3$  units (symbol k). E.g., 1 kg = 1 kilogram = 1,000 grams.

### Kilogram

(1) A mass identical with that of the international kilogram, at the International Bureau of Weights and Measures in France. It is the mass of a liter of water at 4°C.

**Kilogram-equivalent Weight.** A unit of mass 1000 times the gram-equivalent weight.

**Kipp's Apparatus.** Equipment for the production of a gas by interaction of a liquid and a solid. It consists of three receptacles, the top is reservoir for the liquid and is connected to the bottom. The middle contains the solid and a tap for the gas. When gas is released the liquid rises and reacts with the solid, when the tap is closed the back pressure returns the liquid to the lower reservoir and reaction ceases. Once widely used for the production of  $H_2S$  (HCl) and  $FeS$  and  $CO_2$  (HCl and  $CaCO_3$ ).

**Kistiakowsky-fishtine Equation.** An equation to calculate latent heats of vaporization of pure compounds; useful when vapor pressure and critical data are not available.

**Kjeldahl Flask.** A round-bottomed flask with a long, wide neck used in the determination of nitrogen by Kjeldahl's method.

**Kjeldahl Method.** An analytical method for the determination of nitrogen particularly in organic materials. The N is converted to  $NH_4^+$  with conc.  $H_2SO_4$  and catalysts. After neutralization the  $NH_3$  is distilled off (sometimes from a Kjeldahl flask) and estimated by titration after absorption.

**Kjeldahl Test.** An analytical method for determination of nitrogen in certain organic compounds. It involves addition of a small amount of anhydrous potassium sulfate to the test compound, followed by heating the mixture with concentrated sulfuric acid, often with a catalyst such as copper sulfate. As a result ammonia is formed. After alkalyzing the mixture with sodium hydroxide the ammonia is separated by distillation, collected in standard acid and the nitrogen determined by back-titration.

**Klein-rydberg Method.** A method for determining the potential energy function of the distance between the nuclei of a diatomic molecule from the molecule's vibrational and rotational level.

**Klein's Reagent.** A saturated solution of cadmium borotungstate, formula variously given, possibly  $2\text{CdO} \cdot \text{B}_2\text{O}_3 \cdot 18\text{H}_2\text{O}$ . Sp. gr. 3.28.

Hazard : Probably toxic.

Use : Separation of minerals by specific gravity.

**Knockout Vessel.** A vessel, drum, or trap used to remove fluid droplets from flowing gases.

**Knot.** A chiral structure in which rings containing 50 or more members have a knotlike configuration.

**Knudsen Cell.** A vessel used to measure very low vapor pressures by measuring the mass of vapor which escapes when the vessel contains a liquid in equilibrium with its vapor.

**Knudsen-langmuir Equation.** Relationship of molecular distillation rate to vapor saturation pressure, solution temperature, and molecular weight during evaporation and no-recycle condensation.

**Kohlrausch Method.** A method of measuring the electrolytic conductance of a solution using a Wheatstone bridge.

**Kopp's Law.** The law that for solids the molal heat capacity of a compound at room temperature and pressure approximately equals the sum of heat capacities of the elements in the compound.

**Korshun Method.** Microdetermination of carbon and hydrogen in organic compounds; the sample is prepyrolyzed (cracked) in a shortage of oxygen, then oxidized in an excess of oxygen.

**Kossel-sommerfeld Law.** The law that the spectra of the atom and ions belonging to an isoelectronic sequence resemble each other, especially in their multiplet structure.

**Kovat's Retention Indexes.** Procedure to identify compounds in gas chromatography; the behaviour of a compound is indicated by its position on a scale of normal alkane values (for example, methane=100, ethane=200).

**Kremser Formula.** Equation for calculating distillation-column material balances and equilibrium, assuming the ideal distribution law, that is, the concentrations in the two phases (vapor and liquid) are proportional to each other.

**Kundt Rule.** The rule that the optical absorption bands of a solution are displaced toward the red when its refractive index increases because of changes in composition or other causes.

**Kurie Plot.** Graph used in studying beta decay, in which the square root of the number of beta particles whose momenta (or energy) lie within a certain narrow range, divided by a function worked out by Fermi, is plotted against beta-particle energy; it is a straight line for allowed transitions and some forbidden transitions, in accord with the Fermi beta-decay theory. Also known as Fermi plot.

# L

**Lactam.** An internal (cyclic) amide formed by heating gamma ( $\gamma$ ) and delta ( $\delta$ ) amino acids; thus  $\gamma$ -aminobutyric acid readily forms  $\gamma$ -butyrolactam lactam (pyrrolidone); many lactams have physiological activity.

**Lactide.** A cyclic, intermolecular, double ester formed from  $\alpha$ -hydroxy acids; most lactides are relatively low melting solids and are easily hydrolyzed by base to form salts of the parent acid, such as sodium lactate.

**Lactose**  $C_{12}H_{22}O_{11}$ . A disaccharide composed of D-glucose and D-galactose which occurs in milk. Also known as lacticin; milk sugar.

**Lakes.** Insoluble pigments obtained by precipitating natural and artificial colouring matters (dyestuffs, dye-wood extracts, cochineal, etc.) on to suitable bases in the presence of  $Al^{3+}$ , salts of  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Sn^{4+}$  or other metals, and compounds like tannic acid commonly used as mordants in dyeing processes. The preferred bases or substrates are :

- (1)  $Al_2O_3$ , where transparency or richness of colour is desired, as for the manufacture of pigments for use in printing inks;
- (2) china clay, where it is desired to make a light soft product with bulk and good suspension properties;
- (3) barytes,  $BaSO_4$ , which is the most important base for pigments used in paint and linoleum manufacture;
- (4) blanc fixe, precipitated  $BaSO_4$ , which is usually much more finely divided than the natural crystalline barytes;
- (5) green earth and precipitated iron(III) hydroxides which are used according to the colour requirement of the product.



Many pigments of excellent quality and excellent fastness to light are made from artificial dyestuffs; but the lakes formerly made from natural dyestuffs, such as madder and the dye-wood extracts, are no longer in demand, either because they are too costly or because the colour fades. The exceptions are crimson lake (an artists' colour) made from cochineal, and log-wood extracts (containing haematein as the active principle used for dyeing wool and silk black in conjunction with  $\text{Fe(III)}$  and  $\text{Cr(III)}$  salts as mordants).

**Lambert-beer Law.** See Bouguer-Lambert-Beer law.

**Lambert's Law.** See Bouguer-Lambert law.

**Lamb Shift.** A small shift in the energy levels of a hydrogen atom, and of hydrogenlike ions, from those predicted by the Dirac electron theory, in accord with principles of quantum electrodynamics.

### **Lande G Factor**

1. The negative ratio of the magnetic moment of an electron or atom, in units of the Bohr magneton, to its angular momentum, in units of Planck's constant divided by  $2\pi$ .
2. The ratio of the difference in energy between two energy levels which differ only in magnetic quantum number to the product of the Bohr magneton, the applied magnetic field, and the difference between the magnetic quantum numbers of the levels; identical to the first definition for free atoms. Also known as Lande splitting factor; spectroscopic splitting factor.
3. The ratio of the magnetic moment of a nucleon, in units of the nuclear magneton, to its angular momentum in units of Planck's constant divided by  $2\pi$ .

**Lande Interval Rule.** The rule that when the spin-orbit interaction is weak enough to be treated as a perturbation, an energy level having definite spin angular momentum and orbital angular

momentum is split into levels of differing total angular momentum, so that the interval between successive levels is proportional to the larger of their total angular momentum values.

**Lande T-permanence Rule.** The rule that the sum of the shifts of energy levels produced by the spin-orbit interaction, over a series of states having the same spin and orbital angular momentum quantum numbers (or the same total angular momentum quantum numbers for individual electrons) but different total angular momenta, and having the same total magnetic quantum number, is independent of the strength of an applied magnetic field.

**Lande Splitting Factor.** See Lande  $g$  factor.

**Langmuir Isotherm Equation.** An equation, useful chiefly for gaseous systems, for the amount of material adsorbed on a surface as a function of pressure, while the temperature is held constant, assuming that a single layer of molecules is adsorbed; it is  $f = ap/(1 + ap)$ , where  $f$  is the fraction of surface covered,  $p$  is the pressure, and  $a$  is a constant.

**Lanthanum Nitrate**  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  Hygroscopic white crystals melting at  $40^\circ\text{C}$ ; soluble in alcohol and water; used as an antiseptic and in gas mantles.

**Laporte Selection Rule.** The rule that an electric dipole transition can occur only between states of opposite parity.

**Laser.** A device which produces beams of monochromatic light of very great intensity in which the waves are coherent. The name is derived from Light Amplification by Stimulated Emission of Radiation. The theoretical problems in the construction of lasers were first published by Townes and Schawlow, in 1958, and the first optical laser was built in 1960.

Light emitted from an ordinary source, such as a filament lamp, is not of a single wavelength (non-monochromatic) and neither is it coherently phased *i.e.* the wave fronts are out of step with one another. When an atom in its ground state ( $E_0$ )

absorbs energy (photons) it is excited to a higher energy level ( $E_1$ ). The energy absorbed may now be spontaneously released either immediately or after some time to yield the ground state of the atom once more. In a laser, however, the excited atom is struck by a photon of exactly the same energy as the one which would be emitted spontaneously. The excited atom is stimulated to emit a photon and return to the ground condition with the result that two photons of precisely the same wavelength are produced. The process can now be repeated throughout the system.

An example of a solid laser is the ruby crystal ( $\text{Al}_2\text{O}_3$  containing about 0.05% chromium). When the chromium atoms absorb light, they are raised to excited states and revert to their ground state by a two-stage process, (1) by yielding some of their energy to the crystal lattice to give a metastable state, and (2) after a few milliseconds in this state by spontaneously emitting photons of wavelength  $6493 \text{ \AA}$  to return to their original energy level. The laser action takes place when some of the photons emitted from stage (2) stimulate the excited chromium atoms in stage (1) to emit their radiation faster than they normally would and a cascade of photons of wavelength  $6943 \text{ \AA}$  results. The ruby crystal in the form of a rod several centimetres long and about half a centimetre in diameter has ends which are parallel and optically flat. One end is completely silvered, the other partially silvered. The atoms are excited by a powerful electronic flash tube which is placed close to the crystal. As a result of the silvered ends of the ruby, the photons are reflected back and forward many times along the crystal axis, continuously stimulating emission until a coherent beam of light of very high intensity is emitted through the partly silvered end of the crystal.

Many different types of laser materials are now known. Glasses containing neodymium are used for high-out lasers; gas lasers using helium-neon mixtures or caesium vapour have also been made. The most efficient lasers are those using semi-

conductors, with for example gallium arsenide phosphide as the active crystal.

Due to the very high intensity of the laser beams and their coherent nature they may be used in a variety of ways. The beam intensity is such that even a brief flash is sufficient to melt or vapourize very hard materials. A medical application is to 'weld' a torn or injured retina to its support and so prevents its becoming detached. Decayed parts of teeth can be 'removed'. Many advances are possible in the field of telecommunications, and when the efficiency of beam production is increased lasers may be used for cutting and welding processes. Lasers are used commercially for excitation with a specific energy. Isotope separation may be a possibility using laser excitation to decompose compounds of a particular isotope.

**Laser Heterodyne Spectroscopy.** A high-resolution spectroscopic technique, used in astronomical and atmospheric observations, in which the signal to be measured is mixed with a laser signal in a solid-state diode, producing a difference-frequency signal in the radio-frequency range.

**Laser-induced Nuclear Polarization.** A technique for making the spin vectors of an ensemble of nuclei point preferentially in one direction by means of an optical pumping process using either circularly or linearly polarized laser light. Abbreviated LINUP.

**Laser Spectroscopy.** A branch of spectroscopy in which a laser is used as an intense, monochromatic light source; in particular, it includes saturation spectroscopy, as well as the application of laser sources to Raman spectroscopy and other techniques.

**Latent Heat.** The quantity of energy in calories per gram absorbed or given off as a substance undergoes a change of state, that is, as it changes from liquid to solid (freezes), from solid to liquid (melts), from liquid to vapor (boils), or from vapor to liquid (condenses). No change in temperature occurs. Water has unusually high latent heat values; the latent heat of fusion (melting) of ice is 80 cal per gram, and the latent heat of

condensation of steam (latent heat of vaporization of water) (is 540 cal. per gram. The considerable energy delivered by steam condensation is utilized for power generation and for heating a variety of chemical plant equipment (dryers, evaporators, reactors and distillation columns).

**Lattice.** A regular periodic arrangement of points in three-dimensional space; it consists of all those points  $P$  for which the vector from a given fixed point to  $P$  has the form  $n_1 a + n_2 b + n_3 c$ , where  $n_1$ ,  $n_2$ , and  $n_3$  are integers, and  $a$ ,  $b$ , and  $c$  are fixed, linearly independent vectors. Also known as periodic lattice; space lattice.

**Lattice Constant.** A parameter defining the unit cell of a crystal lattice, that is, the length of one of the edges of the cell or an angle between edges. Also known as lattice parameter.

**Lattice Defect.** See crystal defect.

**Lattice Parameter.** See lattice constant.

**Laue Camera.** The apparatus used in the Laue method; the x-ray beam usually enters through a hole in the x-ray film, which records beams bent through an angle of nearly  $180^\circ$  by the crystal; less commonly, the film is placed beyond the crystal.

**Laue Condition**

1. The condition for a vector to lie in a Laue plane; its scalar product with a specified vector in the reciprocal lattice must be one-half of the scalar product of the latter vector with itself.
2. See Lave equations.

**Laue Equations.** Three equations which must be satisfied for an x-ray beam of specified wavelength to be diffracted through a specified angle by a crystal: they state that the scalar products of each of the crystallographic axial vectors with the difference between unit vectors in the directions of the incident and scattered beams, are integral multiples of the wavelength. Also known as Laue condition.

**Laue Method.** A method of studying crystalline structures by x-ray diffraction in which a finely collimated beam of polychromatic x-rays falls on a single crystal whose orientation can be set as desired, and diffracted beams are recorded on a photographic film.

**Laue Pattern.** The characteristic photographic record obtained in the Laue method.

**Laue Plane.** A plane which is the perpendicular bisector of a vector in the reciprocal lattice; such planes form the boundaries of Brillouin zones.

**Laue Theory.** A theory of diffraction of x-rays by crystals, based on the Laue equations.

**Law of Mass Action.** The law stating that the rate at which a chemical reaction proceeds is directly proportional to the molecular concentrations of the reacting compounds.

**LC<sub>50</sub>.** (Lethal concentration, 50%). That quantity of a substance administered by inhalation that is necessary to kill 50% of test animals exposed to it within a specified time. This test applies not only to gases and vapors but to fume, dusts and other particulates suspended in air.

**LCL.** Abbreviation for "less than carload lot"; used by shippers, traffic managers, railroads, etc.

**LD<sub>50</sub>.** (Lethal dose, 50%). That quantity of a substance administered either orally or by skin contact necessary to kill 50% of exposed animals in laboratory tests within a specified time. A substance having an LD<sub>50</sub> of less than 50 mg per kg of body weight is rated highly toxic by toxicologists.

**L Capture.** A type of generalized beta interaction in which a nucleus captures an electron from the L shell of atomic electrons (the shell second closest to the nucleus).

**Lea and Nurse Method.** A method of determining specific surface of fine particles by measuring the pressure drop across a packed bed of particles when a flow of air is passed through the bed.

**Lead Accumulator.** An accumulator consists of a number of plates of Pb, each alternate plate is connected to one wire and the remaining plates to another wire. The plates are covered with a mixture of Pb oxides and Pb sulphate, and are placed in dilute sulphuric acid. When a current is passed through the accumulator  $\text{PbO}_2$  is formed on one set of plates and Pb on the other, and some  $\text{H}_2\text{SO}_4$  is produced. When the accumulator is used to generate electricity  $\text{H}_2\text{SO}_4$  acts on the Pb, the PbO and  $\text{PbO}_2$  forming  $\text{PbSO}_4$  and water to give a potential.

**Leakage.** A phenomenon occurring in an ion-exchange process in which some influent ions are not adsorbed by the ion-exchange bed and appear in the effluent.

**Least Square Method.** It is based on the principle that the best fitting line is the one where the sum of the squares of the deviation is minimum *i.e.*

$$\sum (y - y_{cal})^2 \text{ is minimum.}$$

Mathematically, It has been proved if the derivative of a function is zero, then the value obtained by solving the function is zero.

$$i.e. \quad d = \frac{\sum (y - y_{cal})^2}{dm} = 0$$

Where m is the coefficient of x.

$$d = \frac{\sum (y - mx)^2}{dm} = 0$$

$2\sum (-x)(y - mx) = 0$  which on rearrangement gives,

$$2\sum (-xy) + 2\sum mx^2 = 0$$

$$\text{or } -\sum (xy) + m \sum x^2 = 0$$

$$m = \frac{\sum xy}{\sum x^2}$$

For a st. line not passing through the origin,

$$y = mx + c$$

The set of observation is divided into two groups.

For the two groups.

$$\sum xy = \sum c + m \sum x^2$$

$$\sum' xy = \sum' c + m \sum' x^2$$

The two equations are then solved to find  $m$  and  $c$  which can be best fitted into the straight line graph.

**Leaving Group.** The group of charged or uncharged atoms that departs during a substitution or displacement reaction. Also known as nucleofuge.

**Left-handed.** Having a crystal structure with a mirror-image relationship to a right-handed structure.

**L Electron.** An electron in the L shell.

**Lennard-Jones Potential.** A semiempirical approximation to the potential of the force between two molecules, given by  $V = (A/R^{12}) - (B/R^6)$ , where  $R$  is the distance between the centres of the molecules, and  $A$  and  $B$  are constants.

**Levan** ( $C_6H_{10}O_5$ )<sub>n</sub>. A polysaccharide consisting of repeating units of D-fructose and produced by a range of microorganisms, such as *Bacillus mesentericus*.

**Levigate.**

1. To separate a finely divided powder from a coarser material by suspending in a liquid in which both substances are insoluble. Also known as elutriation.
2. To grind a moist solid to a fine powder.

**Levo Form.** An optical isomer which induces levorotation in a beam of plane polarized light.

**Levorotatory.** Having the property when in solution of rotating the plane of polarized light to the left or counterclockwise. Levorotatory compounds may have the prefix l- to distinguish them from their dextrorotatory or d-isomers, but the minus sign(—) is preferred.

**Lewis Acid.** A substance that can accept an electron pair from a base; thus,  $AlCl_3$ ,  $BF_3$ , and  $SO_3$  are acids.

**Lewis Base.** A substance that can donate an electron pair; examples are the hydroxide ion,  $OH^-$ , and ammonia,  $NH_3$ .



**Lewis-Matheson Method.** Trial-and-error calculation method for the design of multicomponent distillation columns, or for the determination of the separating ability of an existing column.

**Libby Effect.** The increase, since about 1950, in the carbon-14 content of the atmosphere; produced by the detonation of thermonuclear devices.

**Liesegang Rings.** When chemical reaction takes place by double decomposition, one of the reactants in solution diffusing into a gel impregnated with the second reactant, the product, if insoluble, is often deposited, not as a continuous precipitate, but in the form of bands separated by regions of clear gel. These are termed Liesegang rings after their discoverer who first noticed them in the system  $\text{AgNO}_3\text{--K}_2\text{Cr}_2\text{O}_7$  (in gelatin). It is possible to produce Liesegang rings in capillary tubes or porous media without the presence of a gel.

**Life Test.** In petroleum testing, an ASTM oxidation test made on inhibited steam-turbine oils to determine their stability under oxidizing conditions.

**Lift-off.** In gas burners having a stationary flame it is essential that the flame speed of the combustible mixture should be balanced by the velocity of the mixture in the burner tube or flame ports. If the flame speed is too low or the mixture velocity too high the flame can lift-off the burner mouth or flame ports. An increase of inert gases or carbon monoxide in the fuel gas tends to reduce flame speed.

**Ligand.** The molecule, ion, or group bound to the central atom in a chelate or a coordination compound; an example is the ammonia molecules in  $[\text{Co}(\text{NH}_3)_6]^{3+}$ .

**Ligand Membrane.** A solvent immiscible with water and a reagent and acting as an extractant and complexing agent for an ion.

**Lime Water.** (calcium hydroxide solution).

Properties: Clear, colorless, odorless, alkaline aqueous solution of calcium hydroxide containing not less than 0.14 g of  $\text{Ca}(\text{OH})_2$  in each 100 ml at 25°C.

(Note : The strength varies with the temperature at which the solution is stored.) Sp. gr. about 1.00 (25°C). Absorbs carbon dioxide from air.

**Limiting Current.** In polarographic determinations, when potential applied to systems is slowly increased, it reaches a particular value which is sufficient to reduce the metal ions and hence the current increases. This continues till at a particular potential all the ions that diffuse to cathode are reduced. Any further increase in potential does not result in any increase in current. This value of current is called as limiting current.

**Limiting Current Density.** The maximum current density to achieve a desired electrode reaction before hydrogen or other extraneous ions are discharged simultaneously.

**Limiting Viscosity Number.** See intrinsic viscosity.

**Linear Stark Effect.** A splitting of spectral lines of hydrogenlike atoms placed in an electric field; each energy level of principal quantum number  $n$  is split into  $2n-1$  equidistant levels of separation proportional to the field strength.

**Line-formula Method.** A system of notation for hydrocarbons showing the chemical elements; functional groups, and ring systems in linear form; an example is acetone,  $\text{CH}_3\text{COCH}_3$ .

### Line Spectrum

1. A spectrum of radiation in which the quantity being studied, such as frequency or energy, takes on discrete values.
2. Conventionally, the spectra of atoms, ions, and certain molecules in the gaseous phase at low pressures; distinguished from band spectra of molecules, which consist of a pattern of closely spaced spectral lines which could not be resolved by early spectroscopes.

**Line Strength.** The intensity of a spectrum line.

**Liquid Chromatography.** An analytical method based on separation of the components of a mixture in solution by selective adsorption. All systems include a moving solvent; a means of producing solvent motion, such as gravity or (in more recently development equipment) a pump; a means of sample introduction; a fractionating column; and a detector. Innovations in functional systems provide the analytical capability for operating in three separation modes:

1. Liquid/liquid: partition in which separations depend on relative solubilities of sample components in two immiscible solvents (one of which is usually water).
2. Liquid/solid: adsorption where the differences in polarities of sample components and their relative adsorption on an active surface determine the degree of separation.
3. Molecular size separations which depend on the effective molecular size of sample components in solution.

Solvents, often referred to as carriers include isooctane, methyle ethyl ketone, acetone/chloroform, tetrahydrofuran, hexane, and toluene.

Packing materials in columns of various lengths, include silica gel, alumina, glass beads, polystyren gel and ion exchange resins.

**Liquid-liquid Extraction.** A method of extracting a desired component from a liquid mixture by bringing the solution into contact with a second liquid, the solvent, in which the component is also soluble, and which is immiscible with the first liquid or nearly so. Some of the component enters the solvent, forming an extract, while the solution that is left, the raffinate, is depleted in the component by this amount. The two phase are separated and the solvent removed from the component by evaporation or distillation. By repeating the process a number of times all of the component may be extracted.

On an industrial scale liquid-liquid extraction is carried out in either stagewise or differential contact equipment. The

former employs a series of mixer-settler units in each of which the liquids are first contacted and then allowed to separate. Feed and solvent normally flow counter-current to each other through the system. The characteristic of this method is that the liquid compositions change in a series of steps from stage to stage. In differential contact equipment, consisting of such units as spray and packed towers, the compositions of the two phases change continuously as they pass through the equipment.

Liquid-liquid extraction is used for such applications as the removal of phenol from aqueous solution with benzene as solvent, and the removal of aromatics from paraffinic and naphthenic hydrocarbons using liquid sulphur dioxide (Edeleanu process).

**Liquid Chromatography.** A form of chromatography employing a liquid as the moving phase and a solid or a liquid on a solid support as the stationary phase; techniques include column chromatography, gel permeation chromatography, and partition chromatography.

**Liquid Filter.** A device for the removal of solids or coalesced droplets out of a liquid stream by use of a filter medium, such as a screen, cartridge, or granular bed.

**Liquid Junction Emf.** The emf (electromotive force) generated at the area of contact between the salt bridge and the test solution in a pH cell electrode.

**Liquid-liquid Chemical Reaction.** Chemical reaction in which the reactants, two or more, are liquids.

**Liquid-liquid Extraction.** The removal of a soluble component from a liquid mixture by contact with a second liquid, immiscible with the carrier liquid in which the component is preferentially soluble.

**Liquid-phase Hydrogenation.** Hydrogen reaction with liquid-phase hydrogenatable material, such as unsaturated aliphatic or aromatic hydrocarbons.

**Liquid Seal**

1. The depth of liquid above an opening from which gas or vapor issues, as for a riser in a distillation-column tray.
2. Product drawoff in which a depth of liquid prevents the outflow of gas or vapor.

**Liquid-solid Chemical Reaction.** Chemical reaction in which at least one of the reactants is a liquid, and another of the reactants is a solid.

**Liquid-vapor Chemical Reaction.** Chemical reaction in which at least one of the reactants is a liquid, and another of the reactants is a vapor.

**Liquid-vapor Equilibrium.** The equilibrium relationship between the liquid and its vapor phase for a partially vaporized compound or mixture at specified conditions of pressure and temperature; for mixtures, it is expressed by  $K=x/y$ , where  $K$  is the equilibrium constant,  $x$  the mole fraction of a key component in the vapor, and  $y$  the mole fraction of the same key component in the liquid. Also known as vapor-liquid equilibrium.

**Liquor**

1. Supernatant liquid decanted from a liquid-solids mixture in which the solids have settled.
2. Liquid overflow from a liquid-liquid extraction unit.

**Lithium Aluminium Hydride.**  $\text{LiAlH}_4$ . A compound made by the reaction of lithium hydride and aluminium chloride; a powerful reducing agent for specific linkages in complex molecules; used in organic synthesis.

**Lithium Cell.** An electrolytic cell for the production of metallic lithium.

**Lithogeochemical Survey.** A geochemical survey that involves the sampling of rocks.

**Littrow Grating Spectrograph.** A spectrograph having a plane grating at an angle to the axis of the instrument, and a lens in front of the grating which both collimates and focuses the light.

**Littrow Mounting.** The arrangement of the grating and other components of a Littrow grating spectrograph, which is analogous to that of a Littrow quartz spectrograph.

**Littrow Quartz Spectrograph.** A spectrograph in which dispersion is accomplished by a Littrow quartz prism with a rear reflecting surface that reverses the light; lens in front of the prism acts as both collimator and focusing lens.

**Litmus (Lichen blue).**

**Properties :** A blue, amorphous powder (frequently compressed into small cakes or strips ("paper")). Soluble in water; changes color with acidity of solution; red at pH 4.5, blue at pH 8.3.

**Derivation :** By treating lichens (particularly *variolaria lecanora* and *V. roccella*) with ammonia and potash and then fermenting the mass.

**Use :** Indicator in analytical chemistry where precision is not required; soil testing.

**Lixivate.** To extract a soluble component from a solid mixture by washing or percolation processes.

**L/M.** The ratio of the number of internal conversion electrons emitted from the L shell in the de-excitation of a nucleus to the number of such electrons emitted from the M shell.

**Loading.** Condition of vapor overcapacity in a liquid-vapor-contact tower, in which rising vapor lifts or holds falling liquid.

**Loaming.** In geochemical prospecting, a method in which samples of material from the surface are tested for traces of a sought-after metal; its presence on the surface presumably indicates a near-surface ore body.

**Lobry de Bruyn-ekenstein Transformation.** The change in which an aldose sugar treated with dilute alkali results in a mixture of an epimeric pair and 2-keto-hexose due to the production of enolic forms in the presence of hydroxyl ions, followed by a rearrangement.

**Longitudinal Baffle.** Baffle sheets or plates within a process vessel (such as a heat exchanger) that are parallel to the long dimension of the vessel; used to direct fluid flow in the desired flow pattern.

**Longitudinal Flow Reactor.** Theoretical reactor system in which there is no longitudinal mixing (back mixing) of reactants and products as they flow through the reactor, but in which there is complete radial (side-to-side) mixing.

**Long-tube Vertical Evaporator.** A liquid evaporator in which the material is forced into the bottom of a bundle of long, vertical tubes; hot liquid on the outsides of the tubes transfers heat to the rising liquid feed, causing partial evaporation.

**Look Box.** Box with glass windows built into distillation-column rundown lines (or other flow lines) so that the stream of condensate from the condenser can be watched.

**Loomis-wood Diagram.** A graph used to assign lines in a molecular spectrum to the various branches of rotational bands when these branches overlap, in which the difference between observed wave numbers and wave numbers extrapolated from a few lines that apparently belong to one branch are plotted against arbitrary running numbers for that branch.

**Loop Seal.** Antivapor seal for liquid drawoffs from process or storage vessels, liquid drawoff is made to flow through an immersed loop or beneath an obstruction, thus sealing off vapor flow.

**Lorentz Line-splitting Theory.** A theory predicting that when a light source is placed in a strong magnetic field, its spectral lines are each split into three components, one of them retaining the zero-field frequency, and the other two shifted upward and downward in frequency by the Larmor frequency (the normal Zeeman effect).

**Lorentz Theory of Light Sources.** A theory according to which light is emitted by vibrations of electrons, which are damped harmonic oscillators attached to atoms.

**Lorentz Unit.** The unit of reciprocal length used to measure the difference, in wave numbers, between a (zero field) spectrum line and its Zeeman components; equal to  $eH/4mc^2$ , where  $H$  is the magnetic field strength,  $c$  is the speed of light, and  $e$  and  $m$  are the charge and mass of the electron respectively (gaussian units).

**Loschmidt's Number.** The number of molecules of an ideal gas in unit volume at stp; equal to  $2.687 \times 10^{19}$  per  $\text{cm}^3$ .

**Lovibond Tintometer.** An instrument widely used for determining the colour of petroleum and other products by comparing the material with a series of red, yellow and blue standard colour-glasses.

**Low-frequency Spectrum.** Spectrum of atoms and molecules in the microwave region, arising from such causes as the coupling of electronic and nuclear angular momenta, and the Lamb shift.

**Low-temperature Separation.** Liquid condensate recovery from wet gases at temperatures of 20 to  $-20^\circ\text{F}$  ( $-6.7$  to  $-28.9^\circ\text{C}$ ), the temperature range at which the gas-oil separator operates.

**L Shell.** The second shell of electrons surrounding the nucleus of an atom, having electrons whose principal quantum number is 2.

**Luggin Probe.** A device which transmits a significant current density on the surface of an electrode to measure its potential.

**Luminescence.** The emission of visible or invisible radiation unaccompanied by high temperature by any substance as a result of absorption of exciting energy in the form of photons, charged particles, or chemical change. It is a general term which includes both fluorescence and phosphorescence. Special types are chemiluminescence, bioluminescence, electroluminescence, photoluminescence, and triboluminescence. Common examples are light from the firefly, fluorescent lamp tubes and television screens.

**Lundegårdh Vaporizer.** A device used for emission flame photometry in which a compressed air aspirator vaporizes the solution within a chamber; smaller droplets are carried into the fuel-gas



stream and to the burner orifice where the solvent is evaporated, dissociated, and optically excited.

## Lye

1. A solution of potassium hydroxide or sodium hydroxide used as a strong alkaline solution in industry.
2. The alkaline solution that is obtained from the leaching of wood ashes.

**Lyman-alpha Radiation.** Radiation emitted by hydrogen associated with the spectral line in the Lyman series whose wavelength is 1215 angstrom units.

**Lyman Band.** A band in the ultraviolet spectrum of molecular hydrogen, extending from 1250 to 1610 angstrom units.

**Lyman Continuum.** A continuous range of wavelengths (or wave numbers or frequencies) in the spectrum of hydrogen at wavelengths less than the Lyman limit, resulting from transitions between the ground state of hydrogen and states in which the single electron is freed from the atom.

**Lyman Ghost.** A false line observed in a spectroscope as a result of a combination of periodicities in the ruling.

**Lyman Limit.** The lower limit of wavelengths of spectral lines in the Lyman series (912 angstrom units), or the corresponding upper limit in frequency, energy of quanta, or wave number (equal to the Rydberg constant for hydrogen).

**Lyman Series.** A group of lines in the ultraviolet spectrum of hydrogen covering the wavelengths of 1215-912 angstrom units.

**Lyophilization.** Rapid freezing of a material, especially biological specimens for preservation, at a very low temperature followed by rapid dehydration by sublimation in a high vacuum.

# M

**M.** Abbreviation for meter.

**M.** Abbreviation for molar, used to characterize the concentration of a solution. A molar solution contains one mole of a substance in one liter of solution.

**M.** Abbreviation for meta—.

**μM.** Abbreviation for micrometer.

**Mμ.** Abbreviation for milimicron.

**Macroanalysis.** Qualitative or quantitative analysis of chemicals that are in quantities of the order of grams.

**Macronutrient.** An element, such as potassium and nitrogen, essential in large quantities for plant growth.

**Macroporous Resin.** A member of a class of very small, highly cross-linked polymer particles penetrated by channels through which solutions can flow; used as ion exchanger. Also known as macroreticular resin.

**Maerz and Paul Color System.** A dictionary of 7056 different colors in the form of two-impression screen-plate printing on semi-glossy paper.

**Magnesia Mixture.** Reagent used to analyze for phosphorus; consists of the filtered liquor from an aqueous mixture of ammonium chloride, magnesium sulfate, and ammonia.

**Magneson.**  $C_{12}H_9N_3O_4$ . A brownish-red powder, soluble in dilute aqueous sodium hydroxide; used in the detection of magnesium and molybdenum. Also known as 2,4-dihydroxy-4'-nitroazobenzene.

**Magnetic Filter.** Filtration device in which the filter screen is magnetized to trap and remove fine iron from liquids or liquid suspensions being filtered.

**Magnetic Quantum Number.** The eigenvalue of the component of an angular momentum operator in a specified direction, such as that of an applied magnetic field, in units of Planck's constant divided by  $2\pi$ .

**Magnetic Scanning.** The magnetic field sorting of ions into their respective spectrums for analysis by mass spectroscopy; accomplished by varying the magnetic field strength while the electrostatic field is held constant.

**Magnetochemistry.** A subdivision of chemistry concerned with the effect of magnetic fields on chemical compounds; analysis and measurement of these effects (e.g., magnetic moment and magnetic susceptibility) are important tools in crystallographic research and determination of molecular structures. Substances that are repelled by a magnetic field are diamagnetic (water, benzene); those that are attracted are paramagnetic (oxygen, transition element compounds). Diamagnetic materials have only induced magnetic moment; paramagnetic materials have permanent magnetic moment. Magnetochemistry have been useful in detection of free radicals, elucidation of molecular configurations of highly complex compounds, and in its application to catalytic and chemisorption phenomena.

**Magnetohydrodynamics (MHD).** The behavior of high-temperature ionized gases passed through a magnetic field. A power-generating method using MHD involves an open cycle in which hot combustion gases from coal, seeded with cerium or potassium to increase electrical conductivity, constitute the working fluid. These are sent through a nozzle surrounded by a magnet; the electricity induced by movement of the ionized gas through the magnetic field is passed to electrodes, and the gas sent to a steam generator. Efficiency is rated at 50-60%, compared with 40% for conventional fossil fuel plants and 33% for plants using nuclear fuels. Two phase liquid metal systems are being studied as auxiliary units for a number of energy converters. MHD is an important field of expansion of research activity on new sources of energy; its high efficiency and low pollution

factor indicate that it may have a significant future in electric power supply.

**Maillard Reaction.** A reaction in which the amino group in an amino acid tends to form condensation products with aldehydes; believed to cause the Browning reaction when an amino acid and a sugar coexist, evolving a characteristic flavor useful in food preparations.

**Majorana Force.** A force between two nucleons postulated to explain various phenomena, which can be derived from a potential containing an operator which exchanges the nucleons' positions but not their spins.

**Makeup Water.** Water feed needed to replace that which is lost by evaporation or leakage in a closed-circuit, recycle operation.

**Manganate**

1. Salts that have manganese in the anion.
2. In particular, a salt of manganic acid formed by fusion of manganese dioxide with an alkali.

**Manifold of States.** A set of states sufficient to form a representation of an operator or a Lie group of operators.

**Mannan.** Any of a group of polysaccharides composed chiefly or entirely of D-mannose units.

**Manometers.** - Instruments used to measure pressure differences between two points (one may be the atmosphere) in a liquid or a gas. In its simplest form consists of an upright transparent U-tube partially filled with liquid (often Hg); the difference in levels gives the pressure difference directly. Mechanical manometers (using the deflection of a diaphragm) and other devices are more costly but more precise methods of pressure measurement.

**Marangoni Effect.** The effect that a disturbance of the liquid-liquid interface (due to interfacial tension) has on mass transfer in a liquid-liquid extract on system.

**Marsh Gas.** Combustible gas, consisting chiefly of methane, produced as a result of decay of vegetation in stagnant water.

**Marsh Test.** A test for the presence of arsenic in a compound; the substance to be tested is mixed with granular zinc, and dilute hydrochloric acid is added to the mixture; gaseous arsine forms, which decomposes to a black deposit of arsenic, when the gas is passed through a heated glass tube. Also known as Marsh-Berzelius test.

**Mass Action Law.** The law that the rate of a chemical reaction for a uniform system at constant temperature is proportional to the concentrations of the substances reacting. Also known as Guldberg and Waage law.

**Mass-analyzed ion Kinetic Energy Spectrometry.** A type of ion kinetic energy spectrometry in which the ionic products undergo mass analysis followed by energy analysis. Abbreviated MIKES.

**Mass Defect.** The difference between the mass of an atom and the sum of the masses of its individual components in the free (unbound) state.

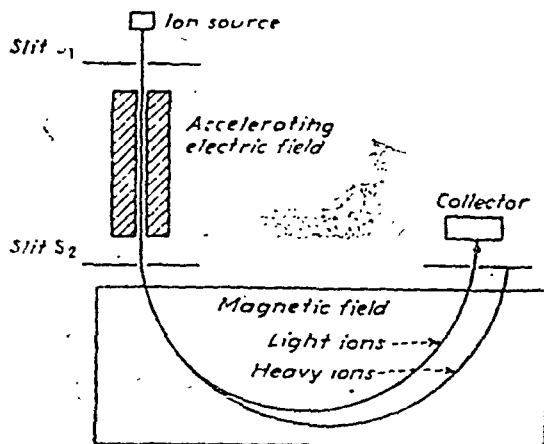
**Massenfilter.** See quadrupole spectrometer.

**Massey Formula.** A formula for the probability that an excited atom approaching the surface of a metal will emit secondary electrons.

**Mass Shift.** The portion of the isotope shift which results from the difference between the nuclear masses of different isotopes.

**Mass Spectrometry.** A method of chemical analysis in which the substance to be analyzed is placed in a vacuum and reduced to low pressure. The resulting vapor is exposed to a beam of electrons which causes ionization to occur, either of the molecules or their fragments. The ions thus produced are accelerated by an electric impulse and then passed through a magnetic field, where they describe curved paths whose

directions depend on the speed and mass-to-charge ratio of the ions. This has the effect of separating the ions according to their mass (electromagnetic separation): Because of their greater kinetic energy, the heavier ions describe a wider arc than the lighter ones, and can be identified on this basis. The ions are collected in appropriate devices as they emerge from the magnetic field.



**Mass Susceptibility.** Magnetic susceptibility of a compound per gram. Also known as specific susceptibility.

**Mass-to-charge Ratio.** In analysis by mass spectroscopy, the measurement of the sample mass as a ratio to its ionic charge.

**Master Batch.** A previously prepared mixture comprised of a base material and a high percentage of an ingredient (usually a dry powder) that is critical to the product being manufactured. Aliquot parts of this mixture are added to production-size quantities (batches) during the mixing operation. This method permits uniform dispersion of very small amounts (less than 1%) of such additives as dry curing agents in rubber and colorants in plastics and paints. Modifying elements may be incorporated in alloys in this way. Master batches of organic dyes dispersed in rubber or plastic are prepared by manufacturers of colorants for direct use. Master-batched accelerators (mixtures of rubber

zinc oxide, and accelerator) are commonly used in rubber mixes.

**Master Equation.** An equation which determines the rate of change of the population of an energy level in terms of the populations of other levels and transition probabilities.

**Masticate.** To process rubber on a machine to make it softer and more pliable before mixing with other substances.

**Material Balance.** A calculation to inventory material inputs versus outputs in a process system.

**Matrix Effects.** The enhancement or suppression of minor element spectral lines from metallic oxides during emission spectroscopy by the matrix element (such as graphite) used to hold the sample.

**Matrix Isolation.** A spectroscopic technique in which reactive species can be characterized by maintaining them in a very cold, inert environment while they are examined by an absorption, electron-spin resonance, or laser excitation spectroscopy.

**Matrix Spectrophotometry.** Spectrophotometric analysis in which the specimen is irradiated in sequence at more than one wavelength, with the visible spectrum evaluated for the energy leaving for each wavelength of irradiation.

**McCabe-Thiele Diagram.** Graphical method for calculation of the number of theoretical plates or contacting stages required for a given binary distillation operation.

**M.C.D.** Magnetic circular dichroism.

**Mean :  $\bar{x}$  :** If  $x_1, x_2, x_3, \dots, x_n$  are the  $n$  observations made, then the mean  $\bar{x}$  of the observation is

$$\bar{x} = \frac{x_1 + x_2 + x_3 + \dots + x_n}{n}$$

**Mean-average Boiling Point.** Pseudo boiling point for a hydrocarbon mixture; calculated from the ASTM distillation curve's volumetric-average boiling point.

**Mean Temperature Difference.** In heat exchange calculations, a pseudo average temperature difference between the warmer and colder fluids at inlet and outlet conditions.

**Mechanophotochemistry.** The study of changes in the dimensions of certain photoresponsive polymers upon exposure to light.

**Media Migration.** Carryover of fibres or other filter material by liquid effluent from a filter unit.

**Median :**  $m$  : If the  $N$  observations are arranged in an ascending order, the middle observations when  $N$  is odd or the mean of the two middle observations when  $N$  is even, is called the median.

### **Medium**

1. The carrier in which a chemical reaction takes place.
2. Material of controlled pore size used to remove foreign particles or liquid droplets from fluid carriers.

**Melting Point.** The melting point or freezing point of a pure substance is the temperature at which its crystals are in equilibrium with the liquid phase at atmospheric pressure. The term "melting point" is used when the equilibrium temperature is approached by heating the solid. Ordinarily melting points refer to temperatures above  $0^{\circ}\text{C}$ , the melting point of ice. The terms melting point and freezing point are often used interchangeably, depending on whether the substance is being heated or cooled. The number of calories required to convert one mole of pure crystals to the liquid state is called the molar heat of fusion.

**M Electron.** An electron whose principal quantum number is 3.

**Meniscus.** The concave curve of a liquid surface in a graduate or narrow tube caused by surface tension. In reading a value (e.g., 5 cc) it is conventional to ignore the higher liquid around the perimeter. In the case of mercury, which does not wet the tube, because of its extremely high surface tension, the meniscus is convex.



**Mercuric-potassium Iodine.** (Mayer's reagent; potassium mercuric iodine). See also Nessler's reagent.  $K_2HgI_4$  or  $2KI.HgI_2$ .

Properties : Odorless, yellow crystals, deliquescent in air. Crystallizes with either 1, 2, or 3 molecules of water. The commercial product is the anhydrous form containing about 25.5% mercury. Sp. gr. 4.29. Neutral or alkaline to litmus. Very soluble in water; soluble in alcohol, ether and acetone.

Derivation :

- (a) Action of hydrochloric acid and potassium iodide on mercuric cyanide or mercuric chloride.
- (b) Action of potassium iodide on mercuric oxide.

Containers : 5-lb and 4-lb bottles.

Hazard: Highly toxic by ingestion, inhalation, and skin absorption. Tolerance (as Hg), 0.05 mg per cubic meter of air.

Use : Analytical chemistry.

Shipping regulation : (Rail, Air) Poison label.

**Mercuric Bromide Reagent.** Arsenic salts form orange or yellow colour with the reagent.

Test Take zinc powder in a semi-micro test tube and add dil.  $H_2SO_4$ . To this add arsenic compound. Hold  $HgB_2$  paper over the mouth of test tube.

A yellow or orange colour indicates arsenic.

**Mercuric Iodide  $HgI_2$**  Poisonous red crystals that turn yellow when heated to  $150^\circ C$ ; soluble in boiling alcohol; used in medicine and in Nessler's and Mayer's reagents.

**Mercury Ammines.** Mercury(II) derivatives, e.g.  $HgCl_2$ , form nitrogen derivatives when treated with ammonia. The products include tetrahedral  $(NH_3)_2HgCl_2$ .  $HgNH_2Cl$  (infusible white precipitate which has a  $Hg-N-Hg-N$ -chain and  $Hg_2NCl$  (the chloride of Millon's base.  $Hg_3NOH.2H_2O$  formed from  $HgO$  and aqueous ammonia) which has a three-dimensional  $Hg_2N$  network with  $OH^-$  and  $H_2O$  in cavities.  $HgNH_2Cl$  is used

medicinally for the treatment of skin diseases. Hg(I) compounds react with ammonia to give a black mixture of Hg and the Hg ammine compounds mentioned above.

**Metal Cluster Compound.** A compound in which two or more metal atoms aggregate so as to be within bonding distance of one another and each metal atom is bonded to at least two other atoms; some nonmetal atoms may be associated with the cluster.

**Metallic Element.** An element generally distinguished (from a nonmetallic one) by its luster, electrical conductivity, malleability, and ability to form positive ions.

**Metastable Equilibrium.** A state of pseudoequilibrium having higher free energy than the true equilibrium state.

**Metastable Ion.** In mass spectroscopy, an ion formed by a secondary dissociation process in the analyzer tube (formed after the parent or initial ion has passed through the accelerating field).

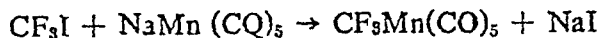
**Metastable Phase.** Existence of a substance as either a liquid, solid, or vapor under conditions in which it is normally unstable in that state.

**Metathesis.** A reaction involving the exchange of elements or groups as in the general equation  $AX + BY \rightarrow AY + BX$ .

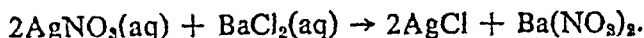
**Metathetical Salts.** Salts that form a four-component, ternary equilibrium system in which there are four possible binary systems, resulting in two quadruple points.

**Metering Pump.** Plunger-type pump designed to control accurately small-scale fluid-flow rates; used to inject small quantities of materials into continuous-flow liquid streams. Also known as proportioning pump.

**Metathetical Reaction.** An exchange reaction, *e.g.*



or



The driving force is generally the insolubility of one of the products in the reaction medium or the volatility of one of the products.

**Methods of Analytical determination :** On the basis of the property measured, analytical methods have been broadly classified into (1) Volumetric, (2) Gravimetric, (3) Optical and (4) Electro-chemical methods. In the Volumetric method, also known as titrimetric analysis a known volume of a solution containing an unknown weight of the desired constituent is made to react with a known volume of a solution whose concentration is known. Volumetric method includes acid-base or neutralisation reactions, precipitation reactions, complexometric titration based on the formation of a complex molecule and oxidation-reduction titrations.

Gravimetric method involves the conversion of a compound of unknown composition into a compound of known composition through precipitation, and then the precipitate is separated by filtration, then dried and quantitatively weighed. Volumetric and Gravimetric methods are the chemical methods of analysis in which the chemical reaction is of prime importance.

Optical and electro chemical methods are the physical or instrumental methods in which the physical property of a substance namely absorption of light, conductivity, heat of reaction, magnetic property etc. is measured to determine the composition of the substance quantitatively. Optical methods include polarimetry, spectrophotometry, and turbidimetry, etc. in which rotation, absorption and scattering of electromagnetic radiations are involved and are measured by a suitable device.

Electrochemical methods include conductometry, potentiometry, polarography, voltametry, amperometry, and coulometry in which changes in conductance, potential difference or emf, current-voltage, voltage, current strength and charge respectively are measured which are related to the concentration of the substances investigated. Electrochemical methods allow a high degree of accuracy due to sophistication of instrumentation

*Methylene Blue*

and provide a means to determine the concentration as low as  $10^{-10}$  A.

Methods based on the heat of reaction include thermometric titrations and thermogravimetry (TG). Thermometric titrations involve measurements of the change of temperature of a solution on addition of a titrant. A plot of temp. versus volume of titrant determines the end point. Thermogravimetry (TG) and differential thermal analysis (DTA) involves the measurement of temp. of a reacting system against weight and enthalpy of the system. The method is based on the fact that at elevated temperatures changes in weight and heat content of the system occurs due to breaking or formation of bonds.

Of the magnetic methods, NMR. (Nuclear magnetic resonance) is of recent one and allows the determination of nuclei which absorb electromagnetic radiations in the microwave region." Measurement of magnetic susceptibility with temperature allows the determination of magnetic characteristics of substances like their Curie point etc.

**Methoxide.** A compound formed from a metal and the methoxy radical; an example is sodium methoxide. Also known as methy-  
late.

**Methoxy** —  $\text{OCH}_3$  — A combining form indicating the oxygen-containing methane radical, found in many organic solvents, insecticides, and plasticizer intermediates.

**Methyl Blue.**  $\text{C}_{37}\text{H}_{37}\text{N}_3\text{O}_3\text{S} \cdot 2\text{NaSO}_3$ . Sodium triphenyl para-rosaniline sulfonate, a dark blue powder or dye used in medicine as an antiseptic and in biological and bacteriological stains. C.I. 42780.

Note : Do not confuse with methylene blue.

**Methyl Dioxolane**  $\text{C}_4\text{H}_7\text{O}_2$ . Water-soluble, clear liquid boiling at  $80^\circ\text{C}$ ; used as a solvent and extractant. Also known as 2-methyl-1,3-dioxolane.

**Methylene Blue** (Methylthionine chloride)  $\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl} \cdot 3\text{H}_2\text{O}$  (medicinal);  $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl})_2 \cdot \text{ZnCl}_2 \cdot \text{H}_2\text{O}$  (dye).

**Properties :** Dark green crystals or powder with bronze-like luster; odorless or slight odor; stable in air. Soluble in water, alcohol, chloroform. Water solutions are deep blue. C.I. 52015.

**Derivation :** By oxidation of para-aminodimethylaniline with ferric chloride in the presence of hydrogen sulfide. The dye is the zinc chloride double salt of the chloride.

**Grades :** U.S.P.; technical.

**Containers :** Bottles, drums.

**Hazard :** Moderately toxic by ingestion.

**Uses :** Dyeing cotton and wool; biological and bacteriological stains; reagent in oxidation-reduction titrations in volumetric analysis; indicator.

**Note :** Do not confuse with methyl blue.

**Methylene Bromide** (dibromomethane)  $\text{CH}_2\text{Br}_2$ . **Properties :** Clear, colorless liquid; sp. gr. 2.47; solidifies  $-52^\circ\text{C}$ ; b.p.  $97^\circ\text{C}$ ; slightly soluble in water; miscible with alcohol, ether, chloroform and acetone. Low toxicity. Nonflammable.

**Methylene Iodide**  $\text{CH}_2\text{I}_2$ . Yellow liquid boiling at  $180^\circ\text{C}$ ; soluble in ether and alcohol, insoluble in water; used as a chemical intermediate and to separate mineral mixtures. Also known as diiodomethane.

**Methyl Ethyl Ketone**, MEK,  $\text{C}_4\text{H}_8\text{O}$ ,  $\text{CH}_3\text{COCH}_2\text{CH}_3$ . Colourless liquid with pleasant odour; b.p.  $80^\circ\text{C}$ . Soluble in water and organic solvents. Occurs with propanone in the products of the destructive distillation of wood. Manufactured by catalytic dehydrogenation or oxidation of 2-butanol. Used extensively as a solvent for vinyl and acrylic resins and cellulose acetate and as an intermediate in the manufacture of methyl isopropenyl ketone and sec-butylamine.

**Methyl Group.** The simplest alkyl group,  $\text{CH}_3$ , formed by dropping a hydrogen atom from methane ( $\text{CH}_4$ ). It occurs at both ends of paraffinic molecules having two or more carbon atoms in the chain, as well as in many other organic compounds.

**Methyl Orange** (para-(para-dimethylamino phenylazo)-benzene sulfonate of sodium; Helianthine B; orange III, gold orange; tropaeolin D) C.I. 13025  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{NNC}_6\text{H}_4\text{SO}_3\text{Na}$ .

Properties : Orange-yellow powder; soluble in hot water, insoluble in alcohol.

Use : Acid-base indicator, red in acid, yellow-orange in alkaline, pH range 3.1—4.4.

**Methylol Urea**  $\text{H}_2\text{NCONHCH}_2\text{OH}$ . Water-soluble, colorless crystals melting at  $111^\circ\text{C}$ ; used to treat textiles and wood, and in the manufacture of resins and adhesives.

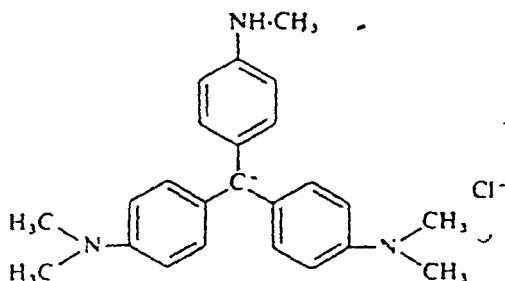
**Methyl Red**  $(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{NNC}_6\text{H}_4\text{COOH}$ . para-dimethylaminoazobenzenecarboxylic acid. C.I. 13020.

Properties : Dark-red powder or violet crystals; m.p.  $180^\circ\text{C}$ ; insoluble in water; soluble in alcohol, ether, glacial acetic acid. Color fades quickly due to reduction.

Use : Acid-base indicator in the range pH 4.2—6.2 (red to yellow).

Note : No longer widely used because of instability.

**Methyl Violet (Basic Violet 1)**. A violet dye obtained by the oxidation of dimethylaniline with  $\text{CuCl}_2$ . It consists of a mixture of the hydrochlorides of tetra-, penta and hexamethyl-p-rosanilines. The formula given is of the pentamethyl compounds :



It is used in dyeing jute, for colouring methylated spirits, as a bacteriological stain and as an indicator, pH range 0.1 (yellow) to 3-2 (violet).

Gentian violet is the name that used to be given to a mixture of the hydrochlorides of penta- and hexamethyl-p-rosanilines. The name is now used only in pharmacy, where it usually refers to methyl violet.

**Microanalysis.** Identification and chemical analysis of material on a small scale so that specialized instruments such as the microscope are needed; the material analyzed may be on the scale of 1 microgram.

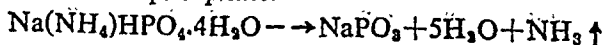
**Microbalance.** A balance capable of detecting and measuring changes in weight of the order of  $10^{-6}$ g or less. For ordinary quantitative analysis on the small scale, the microbalances in use generally weigh up to about 10g, and are sensitive to a change of  $10^{-6}$ g. For special purposes balances have been constructed which are sensitive to as little as  $10^{-11}$ g, but the maximum load is corresponding smaller than that of the ordinary analytical microbalance. Electro-microbalances are systems where the displacement is nullified electrically. Such balances are easier to operate and much more robust than conventional microbalances.

**Microcapsule.** A capsule with a plastic or waxlike coating having a diameter anywhere from well below 1 micrometer to over 2000 micrometers.

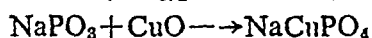
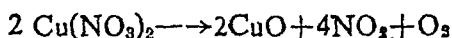
**Microchemistry.** A branch of analytical chemistry that involves procedures that require handling of very small quantities of materials. Specifically, it refers to carrying out various chemical operations (weighting, purification, quantitative and qualitative analysis) on samples ranging from 0.1 to 10 milligrams; this often involves use of a microscope, and still more often of chromatography (q.v.).

**Microcosmic Bead Test.** The microcosmic salt,  $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$  behaves as borax, therefore, it can be used as borax.

**Principle.** When microcosmic salt is heated, it loses water and ammonia and give a clear and transparent bead consisting of sodium metaphosphate.



Sodium metaborate combines with metal oxides to form orthophosphate which possess characteristic colours.



copper orthophosphate

(green when hot and blue when cold in oxidizing flame).

Draw the inference from Table.

### Microcosmic Bead Test

Colour of the bead in oxidizing flame		Colour of the bead in reducing flame		Inference
When hot	When cold	When hot	When cold	
1. Green	Blue	Colourless	Red	Copper
2. Green	Green	Green	Green	Chromium
3. Blue	Blue	Blue	Blue	Cobalt
4. Yellowish brown	Yellow	Yellow	Yellow	Iron
5. Violet	Violet	Colourless	Colourless	Manganese
6. Brown	Brown	Grey	Grey	Nickel

**Microdensitometer.** A high-sensitivity densitometer used in spectroscopy to detect spectrum lines too faint on a negative to be seen by the human eye.

**Microelectrolysis.** Electrolysis of small quantities of material.

**Microelectrophoresis.** Direct microscopic observation and measurement of the velocity of migration of ions or other charged bodies through a solution toward oppositely charged electrodes. Also known as optical cytopherometry.

**Microencapsulation.** Enclosing of materials in capsules from well below 1 micrometer to over 2000 micrometers in diameter.



**Microincineration.** Reduction of small quantities of organic substances to ash by application of heat.

**Micronutrient.** Trace elements and compounds required by living systems only in minute amounts.

**Microporous Barrier.** A metallic or plastic membrane with micrometer-sized pores used for dialysis and other membrane-separation processes.

**Microprobe.** An instrument for chemical microanalysis of a sample, in which a beam of electrons is focused on an area less than a micrometer in diameter, and the characteristic x-rays emitted as a result are dispersed and analyzed in a crystal spectrometer to provide a qualitative and quantitative evaluation of chemical composition.

**Microprobe Spectrometry.** Microanalysis of a sample, using a microprobe.

**Micro Qualitative Analysis.** In micro analysis (commonly called as spot test analysis) the masses and volumes for analysis are about 5 mg and 0.1 ml, *i.e.* 1-2 drops. Tananaev (1920) introduced this technique and Fiegl extended its scope to such an extent that it occupies very important position in the modern qualitative analysis. Selective and characteristic spot tests for inorganic and organic compounds are known which detect with certainty the individual cations present in a mixture.

#### Procedure

- (1) The spot test is carried out either on a plate called spot plate or on a Whatmann filter paper No. 120 or Schleicher and Schull paper No. 601. On the plate it is confined to a small area and takes the shape of spot.
- (2) Take 1-2 drops of the original solution on spot plate followed by systematic addition of the reagent.
- (3) The detail of the test is given in the test of individual cation.

### Advantages

- (1) These are quicker and easier to carry out.
- (2) These can be interpreted more readily.
- (3) These are less susceptible to slight variation of experimental conditions.

### Notes

- (1) The analytical grade reagents must be used.
- (2) The test should be performed strictly according to the instructions provided in a test.

**Microscopy, Chemical.** Use of a microscope primarily for study of physical structure and identification of materials. This is especially useful in forensic chemistry and police laboratories. Many types of microscopes are used in industry; most important are the optical, ultra-, polarizing, stereo-scopic, electron, and x-ray microscopes. Organic dyes of various types are used to stain samples for precise identification.

**Microspectrograph.** A microspectroscope provided with a photographic camera or other device for recording the spectrum.

**Microspectrophotometer.** A split-beam or double-beam spectrophotometer including a microscope for the localization of the object under study, and capable of carrying out spectral analyses within the dimensions of a single cell.

**Microspectroscope.** An instrument for analyzing the spectra of microscopic objects, such as living cells, in which light passing through the sample is focused by a compound microscope system, and both this light and the light which has passed through a reference sample are dispersed by a prism spectroscope, so that the spectra of both can be viewed simultaneously.

**Microwave Spectrometer.** An instrument which makes a graphical record of the intensity of microwave radiation emitted or absorbed by a substance as a function of frequency, wavelength, or some related variable.

**Microwave Spectroscopy.** An instrument used to observe the intensity of microwave radiation emitted or absorbed by a substance as a function of frequency, wavelength, or some related variable.

**Microwave Spectroscopy.** A type of absorption spectroscopy used in instrumental chemical analysis which involves use of that portion of the electromagnetic spectrum having wavelengths in the range between the far infrared and the radiofrequencies, *i.e.*, between 1 millimeter and 30 centimeters. Substances to be analyzed are usually in the gaseous state. Klystron tubes are used as microwave source.

**Microwave Spectrum.** A display, photograph, or plot of the intensity of microwave radiation emitted or absorbed by a substance as a function of frequency, wavelength, or some related variable.

**Migration Current.** Additional current produced by electrostatic attraction of cations to the surface of a dropping electrode; an unpredictable and undesirable effect to be avoided during analytical voltammetry.

**Milk Factor.** A filtrable, noncellular agent in the milk and tissues of certain strains of inbred mice; transmitted from the mother to the offspring by nursing. Also known as Bittner milk factor.

**Miller Indices.** Three integers identifying a type of crystal plane; the intercepts of a plane on the three crystallographic axes are expressed as fractions of the crystal parameters the reciprocals of these fractions, reduced to integral proportions, are the Miller indices. Also known as crystal indices.

**Miller Law.** If the edges formed by the intersections of three faces of a crystal are taken as the three reference axes, then the three quantities formed by dividing the intercept of a fourth face with one of these axes by the intercept of a fifth face with the same axis are proportional to small whole numbers, rarely exceeding 6. Also known as law of rational intercepts.

- Millibarn.** A unit of cross section equal to one-thousandth of a barn.
- Milliequivalent.** One-thousandth of a compound's or an element's equivalent weight.
- Millimicron ( $m\mu$ ).** One-thousandth micron; 10 angstrom units; 1 billionth meter; 1 nanometer.
- Million's Reagent.** Reagent used to test for proteins; made by dissolving mercury in nitric acid, diluting, then decanting the liquid from the precipitate.
- Mineralogy.** The science which concerns the study of natural inorganic substances called minerals.
- Minimum Reflux Ratio.** The smallest reflux ratio in a two-component liquid distillation system that will produce the desired overhead and bottom compositions.
- Minimum Wetting Rate.** The smallest liquid-flow rate through a packed column that will thoroughly wet the column packing.
- Miscibility.** The tendency or capacity of two or more liquids to form a uniform blend, that is, to dissolve in each other; degrees are total miscibility, partial miscibility, and immiscibility.
- Mixed Acid (nitrating acid).** A mixture of sulfuric and nitric acids used for nitrating, *e.g.*, in the manufacture of explosives, plastics, etc. Consists of 36% nitric acid and 61% sulfuric acid.
- Mixed Aniline Point.** The minimum temperature at which a mixture of aniline, heptane, and hydrocarbon will form a solution; related to the aromatic character of the hydrocarbon.
- Mixed Indicator.** The use of a mixture of type or more indicators in order to sharpen the colour change or to restrict the pH range (etc.) over which the colour change occurs.
- Mixed Indicator.** Color-change indicator for acid-base titration end points in which a mixture of two indicator substances is used to give sharper end point color changes.

**Mixed Potential.** The electrode potential of a material while more than one electrochemical reaction is occurring simultaneously.

**Mixer-settler.** Solvent-extraction system with alternating or combined arrangement of mixers and settlers, used for chemicals extraction, lubricating-oil refining, and uranium oxide recovery. Also known as mixer-settler extractor.

**Mixer-settler Extractor.** See mixer-settler.

**MMSCFD.** Abbreviation for million standard cubic feet per day; usually refers to gas flow.

**MMSCFM.** Abbreviation for million standard cubic feet per hour; usually refers to gas flow.

**MMSCFM.** Abbreviation for million standard cubic feet per minute; usually refers to gas flow.

**Modified Lewis Acid.** An acid that is a halide ion acceptor.

**Modulated Raman Scattering.** Application of modulation spectroscopy to the study of Raman scattering; in particular, use of external perturbations to lower the symmetry of certain crystals and permit symmetry-forbidden modes, and the use of wavelength modulation to analyze second-order Raman spectra.

**Modulation Spectroscopy.** A branch of spectroscopy concerned with the measurement and interpretation of changes in transmission or reflection spectra induced (usually) by externally applied perturbation, such as temperature or pressure change, or an electric or magnetic field.

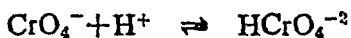
**Mohr Cubic Centimeter.** A unit of volume used in saccharimetry, equal to the volume of 1 gram of water at a specified temperature, usually 17.5°C, in which case, it is equal to 1.00238 cubic centimeters.

**Mohr's Method of Determining End Point in Precipitation Titrations.** In this method  $\text{AgNO}_3$  is titrated with  $\text{KCl}$  solution using  $\text{K}_2\text{CrO}_4$  as an indicator. At the equivalence point chromate ions combine with silver ions forming sparingly soluble red

silver chromate. At the end point the fractional precipitation of two sparingly soluble salts take place. Which precipitate is precipitated first will be determined from their solubility products. The solubility products for  $\text{AgCl} = 1.2 \times 10^{-10}$  and silver chromate  $1.7 \times 10^{-12}$  respectively. When  $\text{Ag}^+$  ions are added to the solution containing  $\text{Cl}^-$  ions and  $\text{CrO}_4^{2-}$  ions, the solubility products of the less soluble salt is reacted first and that salt precipitates completely before the solubility product of more soluble salt is reached. In this case  $\text{AgCl}$  is precipitated first and then  $\text{Ag}_2\text{CrO}_4$ . as.  $\text{AgCl}$  is less soluble. When all the  $\text{Cl}^-$  ions are precipitated by  $\text{AgNO}_3$  then an addition of first slight excess of  $\text{Ag}^+$  ions beyond the equivalence point,  $\text{Ag}^+$  ions react with  $\text{CrO}_4^{2-}$  ions producing intensely red silver chromate.

This titration has the following drawbacks :

1. To make the colour of the precipitate visible, some  $\text{Ag}_2\text{CrO}_4$  must be present.
2. As  $\text{AgCl}$  is present in large excess,  $\text{Ag}^+$  ions will be added to precipitate  $\text{Ag}_2\text{CrO}_4$  clearly.
3.  $\text{CrO}_4^{2-}$  ions give intense yellow colour which makes difficult to identify the red colour of  $\text{Ag}_2\text{CrO}_4$ .
4. The reaction should be carried out in neutral or slightly alkaline medium as high acidic medium may convert chromate ions into dichromate ions.



5. In highly alkaline medium, some  $\text{AgOH}$  may be precipitated. Hence the titration is carried out in the pH range of 7-10.

**Mohr's Salt,  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ .** Iron ammonium sulphate.

**Mohr Titration.** Titration with silver nitrate to determine the concentration of chlorides in a solution; silver chromate precipitation is the end-point indicator.

**Mohs Scale.** A scale of hardness of minerals, introduced by the German mineralogist Friedrich Mohs about 1800. It ranges

from 1 to 10, with talc the softest and diamond the hardest. Each mineral in the scale will scratch all those below it. The steps are not of equal value; the difference in hardness between 9 and 10 is much greater than between 1 and 2.

Diamond	10	Apatite	5
Corundum	9	Fluorite	4
Topaz	8	Calcite	3
Quartz	7	Gypsum	2
Orthoclase(Feldspar)	6	Talc	1

A recent addition is 11 (fused zirconia).

**Moiety.** A part or portion of a molecule, generally complex, having a characteristic chemical or pharmacological property.

**Moisture.** Water that is dispersed through a gas in the form of water vapor or small droplets, dispersed through a solid, or condensed on the surface of a solid.

**Mol.** See mole.

**Molal.** A concentration in which the amount of solute is stated in moles and the amount of solvent in kilograms. The unit of molality is moles of solute per kilogram of solvent and is designated by a small *m*; 1 mole of NaCl in 1 kg of solvent is a 1 molal concentration.

**Note :** Do not confuse with molar).

**Molal Average Boiling Point.** A pseudo boiling point for a mixture calculated as the summation of individual mole fraction boiling point (in degrees Rankine) products.

**Molal Heat Capacity.** See molar heat capacity.

**Molality.** Concentration given as moles per 1000 grams of solvent.

**Molal Quantity.** The number of moles (gram-molecular weights) present, expressed with weight in pounds, grams, or such units, numerically equal to the molecular weight; for example, pound-mole, gram-mole.

**Molal Solution.** Concentration of a solution expressed in moles of solute divided by 1000 grams of solvent.

**Molal Volume.** See molar volume.

**Molar.** A concentration in which one molecular weight in grams (one mole) of a substance is dissolved in enough solvent to make one litre of solution. Molarity is indicated by an italic capital *M*. Molar quantities are proportional to the molecular weights of the substance.

**Molar Conductivity.** The ratio of the conductivity of an electrolytic solution to the concentration of electrolyte in moles per unit volume.

**Molar Heat Capacity.** The amount of heat required to raise 1 mole of a substance  $1^{\circ}$  in temperature. Also known as molal heat capacity molecular heat capacity.

**Molarity.** Measure of the number of gram-molecular weights of a compound present (dissolved) in 1 liter of solution; it is indicated by *M*, preceded by a number to show solute concentration.

**Molar Solution.** Aqueous solution that contains 1 mole (gram-molecular weight) of solute in 1 liter of the solution.

**Molar Specific Heat.** The ratio of the amount of heat required to raise the temperature of 1 mole of a compound  $1^{\circ}$ , to the amount of heat required to raise the temperature of 1 mole of a reference substance, such as water,  $1^{\circ}$  at a specified temperature. Also known as molal specific heat; molecular specific heat.

**Molar Susceptibility.** Magnetic susceptibility of a compound per gram-mole of that compound.

**Molar Volume.** The volume occupied by one mole of a substance in the form of a solid liquid, or gas. Also known as molal volume; mole volume.

**Mole.** An amount of substance of a system which contains as many elementary units as there are atoms of carbon in 0.012 kilogram of the pure nuclide carbon-12; the elementary unit must be specified and may be an atom, molecule ion, electron, photon, or even a specified group of such units.



**Molecular Conductivity.** The conductivity of a volume of electrolyte containing 1 mole of dissolved substance.

**Molecular Diamagnetism.** Diamagnetism of compounds, especially organic compounds whose susceptibilities can often be calculated from the atoms and chemical bonds of which they are composed.

**Molecular Dipole.** A molecule having an electric dipole moment, whether it is permanent or produced by an external field.

**Molecular Distillation (high vacuum distillation)** Distillation at low pressures of the order of 0.001 mm. A molecular distillation is distinguished by the fact that the distance from the surface of the liquid being vaporized to the condenser is less than the mean free path (the average distance travelled by a molecule between collisions) of the vapor at the operating pressure and temperature. This distance is usually of the order of magnitude of a few inches. This process is useful in separation of extremely high boiling and heat sensitive materials such as glycerides and some vitamins.

**Molecular Energy Level.** One of the states of motion of nuclei and electrons in a molecule, having a definite energy, which is allowed by quantum mechanics.

**Molecular Exclusion Chromatography.** See gel filtration.

**Molecular Heat Capacity.** See molar heat capacity.

**Molecularity.** In a chemical reaction, the number of molecules which come together and form the activated complex.

**Molecular Paramagnetism.** Paramagnetism of molecules, such as oxygen, some other molecules, and a large number of organic compounds.

**Molecular Polarizability.** The electric dipole moment induced in a molecule by an external electric field, divided by the magnitude of the field.

**Molecular Relaxation.** Transition of a molecule from an excited energy level to another excited level of lower energy or to the ground state.

**Molecular Sieve.** A group of adsorptive desiccants which are crystalline aluminosilicate materials, chemically similar to clays and feldspars and belonging to a class of minerals known as zeolites (q v.). The outstanding characteristic of these materials is their ability to undergo dehydration with little or no change in crystal structure. The dehydrated crystals are interlaced with regularly spaced channels of molecular dimensions, which comprise almost 50 per cent of the total volume of crystals

The empty cavities in activated "molecular sieve" crystals have a strong tendency to recapture the water molecules that have been driven off. This tendency is so strong that if no water is present they will accept any material that can get into the cavity. However, only those molecules that are small enough to pass through the pores of the crystal can enter the cavities and be adsorbed on the interior surface. The sieving or screening action, which makes it possible to separate smaller molecules from larger ones, is the most unusual characteristic of molecular sieves. They are used in many fields of technology: to dry gases and liquids; for selective molecular separations based on size and polar properties; as ion-exchanges; as catalysts; as chemical carriers; in gas chromatography; and in the petroleum industry to remove normal paraffins from distillates.

**Molecular Specific Heat.** See molar specific heat.

**Molecular Spectroscopy.** The production, measurement, and interpretation of molecular spectra.

**Molecular Spectrum.** The intensity of electromagnetic radiation emitted or absorbed by a collection of molecules as a function of frequency, wave number, or some related quantity.

**Molecular Structure.** The manner in which electrons and nuclei interact to form a molecule, as elucidated by quantum mechanics and a study of molecular spectra.

**Molecular Vibration.** The theory that all atoms within a molecule are in continuous motion, vibrating at definite frequencies specific to the molecular structure as a whole as well as to

groups of atoms within the molecule; the basis of spectroscopic analysis.

**Molecular Volume.** The volume that is occupied by 1 mole (gram-molecular weight) of an element or compound; equals the molecular weight divided by the density.

**Molecular Weight.** The weight of one molecule referred to the standard of  $^{12}\text{C}=12.000$  amu. It is a ratio. The molecular weight is equal to the sum of the atomic weight of the constituent nuclei. The molecular weight expressed in grams is known as the gram molecular weight.

**Molecular-weight Distribution.** Frequency of occurrence of the different molecular-weight chains in a homologous polymeric system.

**Molecule.** A group of atoms held together by chemical forces; the atoms in the molecule may be identical as in  $\text{H}_2$ ,  $\text{S}_2$ , and  $\text{S}_8$ , or different as in  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ; a molecule is the smallest unit of matter which can exist by itself and retain all its chemical properties.

**Mole Fraction.** The ratio of the number of moles of a substance in a mixture or solution to the total number of moles of all the components in the mixture or solution.

**Mole Percent.** Percentage calculation expressed in terms of moles rather than weight.

**Mole Volume.** See molar volume.

**Monatomic.** Composed of one atom.

**Monobasic.** Descriptive of acids having one displaceable hydrogen atom per molecule; acids having two, three or more displaceable H atoms are called dibasic, tribasic, and polybasic, respectively.

**Monochromator.** A spectrograph in which a detector is replaced by a second slit, placed in the focal plane, to isolate a particular narrow band of wavelengths for refocusing on a detector or experimental object.

**Monomer.** A simple molecule which is capable of combining with a number of like or unlike molecules to form a polymer; it is a repeating structure unit within a polymer.

**Mooney Unit.** An arbitrary unit used to measure the plasticity of raw, or unvulcanized rubber; the plasticity in Mooney units is equal to the torque, measured on an arbitrary scale, on a disk in a vessel that contains rubber at a temperature of 100°C and rotates at two revolutions per minute.

**Morse Equation.** An equation according to which the potential energy of a diatomic molecule in a given electronic state is given by a Morse potential

**Morse Potential.** An approximate potential associated with the distance  $r$  between the nuclei of a diatomic molecule in a given electronic state; it is  $V(r) = D\{1 - \exp[-a(r - r_e)]\}^2$ , where  $r_e$  is the equilibrium distance,  $D$  is the dissociation energy, and  $a$  is a constant.

**Moseley's Law.** The law that the square-root of the frequency of an x-ray spectral line belonging to a particular series is proportional to the difference between the atomic number and a constant which depends only on the series.

**Mossbauer Effect.** A nuclear phenomenon discovered in 1957. Defined as the elastic (recoil-free) emission of a gamma particle by the nucleus of a radioactive isotope and the subsequent absorption (resonance scattering) of the particle by another atomic nucleus. Occurs in crystalline solids and glasses, but not in liquids. Examples of gamma-emitting isotopes are: iron 57, nickel 61, zinc 67, tin 119. The Mossbauer effect is used to obtain information on isomer shift, on vibrational properties and atomic motions in a solid, and on location of atoms within a complex molecule.

**Mossbauer Spectroscopy.** The study of Mossbauer spectra, for example, for nuclear hyperfine structure, chemical shifts, and chemical analysis.

**Mossbauer Spectrum.** A plot of the absorption, by nuclei bound in a crystal lattice, of gamma rays emitted by similar nuclei in a second crystal, as a function of the relative velocity of the two crystals.

**Mother.** A mother liquor is a concentrated solution from which the product is obtained by evaporation and/or crystallization, e.g., in sugar manufacture.

**Moving Bed.** Granulated solids in a process vessel that are circulated (moved) either mechanically or by gravity flow; used in catalytic and absorption processes.

**Moving-boundary Electrophoresis.** A U-tube variation of electrophoresis analysis that uses buffered solution so that all ions of a given species move at the same rate to maintain a sharp, moving front (boundary).

**MSCFD.** Abbreviation for thousand standard cubic feet per day; usually refers to gas flow.

**MSCFH.** Abbreviation for thousand standard cubic feet per hour; usually refers to gas flow.

**MSCFM.** Abbreviation for thousand standard cubic feet per minute; usually refers to gas flow.

**M Shell.** The third layer of electrons about the nucleus of an atom, having electrons characterized by the principal quantum number 3.

**Muffle Furnace.** A furnace or kiln in which the materials being heated are kept out of direct contact with the heat source, the combustion being effected by heat reflected from the walls of the furnace.

**Mull Technique.** Method for obtaining infrared spectra of materials in the solid state; material to be scanned is first pulverized, then milled with mineral oil.

**Multiphase Flow.** Mixture of two or more distinct phases (such as oil, water, and gas) flowing through a closed conduit.

## *Murphree Efficiency*

**Multiphoton Absorption.** The excitation of an atom or other microscopic system to a higher quantum state by simultaneous absorption of two or more photons which together provide the necessary energy.

**Multiphoton Ionization.** The removal of one or more electrons from an atom or other microscopic system as the result of simultaneous absorption of two or more photons.

**Multiple Cartridges.** Filter medium made up of two or more filter cartridges, either fastened end to end or arranged side by side (in series or parallel flow respectively).

**Multiple-effect Evaporation.** Series-operation energy economizer system in which heat from the steam generated (evaporated liquid) in the first stage is used to evaporate additional liquid in the second stage (by reducing system pressure), and so on, up to 10 or more effects; commonly used in the pulp and paper industry.

**Multiplet.** A collection of relatively closely spaced spectral lines resulting from transitions to or from the members of a multiplet (as in the quantum-mechanics definition).

**Multiplet Intensity Rules.** Rules for the relative intensities of spectral lines in a spin-orbit multiplet, stating that the sum of the intensities of all lines which start from a common initial level, or end on a common final level, is proportional to  $2J+1$ , where  $J$  is the total angular momentum of the initial level or final level respectively.

**Muriatic Acid.** An old name for hydrochloric acid, still occasionally used in industry. Potassium chloride is sometimes called 'muriate of potash'.

**Murphree Efficiency.** In a plate-distillation column, the ratio of the actual change in vapor composition when the vapor passes through the liquid on a tray (plate) to the composition change of the vapor if it were in vapor-liquid equilibrium with the tray liquid.

**Mutarotation.** A change in the optical rotation of light that takes place in the solutions of freshly prepared sugars.

**Mutual Exclusion Rule.** The rule that if a molecule has a center of symmetry, then no transition is allowed in both its Raman scattering and infrared emission (and absorption), but only in one or the other.

**Mutuality of Phases.** The rule that if two phases, with respect to a reaction, are in equilibrium with a third phase at a certain temperature, then they are in equilibrium with respect to each other at that temperature.

## N

**N.** See newton; nitrogen; normality.

**Nadir Point.** Photograph nadir.

**Nano-** Prefix meaning  $10^{-9}$  unit (symbol n). 1 ng=1 nanogram=0.000000001 gram; 1 nanometer=1 millimicron.

**$\alpha$ -Naphthol**  $C_{10}H_7OH$ . Colourless to yellow powder, melting at  $96^{\circ}C$ ; used to make dyes and perfumes, and in synthesis of organic molecules. Also known as 1-hydroxynaphthalene; 1-naphthol.

**$\beta$ -Naphthol**  $C_{10}H_7OH$ . White crystals that melt at  $121.6^{\circ}C$ ; insoluble in water; used to make pigments, dyes, and antioxidants. Also known as 2-hydroxynaphthalene; 2-naphthol.

**Naphthoresorcinol**  $C_{10}H_6(OH)_2$ . Crystals with a melting point of  $124-125^{\circ}C$ ; soluble in ether, alcohol, and water; used as a reagent for sugars and oils, and to determine glucuronic acid in urine. Also known as 1, 3-dihydroxy-naphthalene.

**Native.** Pertaining to an element found in nature in a nongaseous state.

**Native Metal.** A metallic native element; includes silver, gold, copper, iron, mercury, iridium, lead, palladium, and platinum.

**N-d—M Analysis.** An important method for the structural group analysis of petroleum fractions. Based on the correlation of results obtained by a direct hydrogenation method, it involves the determination of refractive index, density and mean molecular weight of the fraction being analysed. By using equations or a nomogram, results are obtained for the %C in paraffinic, naphthenic and aromatic structures, as well as aromatic and naphthenic rings per mean molecule. A similar method (the  $V_K$ -n-d method) replaces molecular weight by the logarithm of the kinematic viscosity.

**Near-infrared Spectrophotometry.** Spectrophotometry at wavelengths in the near-infrared region, generally using instruments with quartz prisms in the monochromators and lead sulfide photoconductor cells as detectors to observe absorption bands which are harmonics of bands at longer wavelengths.

**Neel Point.** The temperature at which magnetic susceptibility becomes normal.

**N Electron.** An electron in the fourth (N) shell of electrons surrounding the atomic nucleus, having the principal quantum number 4.

**Nephelometry.** A method of quantitative analysis which involves the spectrophotometric estimation of the scattering of light by a colloidal suspension of a precipitate.

**Neutral Red (toluylene red)**  $(CH_3)_2NC_6H_3N_2C_6H_2CH_2NH_2 \cdot HCl$  (tricyclic). 3-Amino-7-(dimethylamino)-2-methylphenazine monohydrochloride. C.I. No. 50040.

Properties : Green powder; dissolves in water or alcohol to give red color.



Use : Acid-base indicator in the range pH 6.8—8.0 (red in acid, yellow brown in alkali); biological stain.

**Nernst Equation.** The relationship showing that the electromotive force developed by a dry cell is determined by the activities of the reacting species, the temperature of the reaction, and the standard free-energy change of the overall reaction.

**Nernst-thomson Rule.** The rule that in a solvent having a high dielectric constant the attraction between anions and cations is small so that dissociation is favored, while the reverse is true in solvents with a low dielectric constant.

**Nernst Zero or Potential.** An electrode potential corresponding to the reversible equilibrium between hydrogen gas at a pressure of 1 standard atmosphere and hydrogen ions at unit activity.

**Nessler's Reagent.** An alkaline solution of  $\text{HgI}_2$  in  $\text{KI}$  used for detecting the estimating ammonia (brown colour or precipitate formed).

**Nessler Tubes.** Cylinders of thin glass, generally graduated, used for comparing turbidities and colours of solutions.

**Neutral Flame.** Gas flame produced by a mixture of fuel and oxygen so as to be neither oxidizing nor reducing.

**Neutralization Equivalent.** For an acid or base, the same as equivalent weight; multiplication of the neutralization equivalent by the number of acidic or basic groups in the molecule gives the molecular weight.

**Neutralization Number.** Petroleum product test; it is the milligrams of potassium hydroxide required to neutralize the acid in 1 gram of oil; used as an indication oil acidity.

**Neutralize.** To make a solution neutral (neither acidic nor basic, pH of 7) by adding a base to an acidic solution, or an acid to a basic solution.

**Neutral Red**  $(\text{CH}_3)_2\text{NC}_6\text{H}_3\text{N}_2\text{C}_6\text{H}_2\text{CH}_2\text{NH}_2.\text{ClH}$  Water- and alcohol-soluble green powder; used as pH 6.8—8.0 acid-base indicator, (DAC—15)

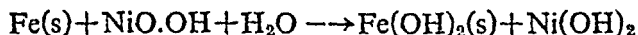
and as a dye to test stomach function. Also known as dimethyl diaminophenazine chloride; toluylene red.

**Neutron Spectrometry.** A method of observing excited states of nuclei in which neutrons are used to bombard a target, causing nuclei to be transmuted into excited states by various nuclear reactions; the resultant excited states are determined by observing resonances in the reaction cross sections or by observing spectra of emitted particles or gamma rays. Also known as neutron spectroscopy.

**Neutron Spectroscopy.** See neutron spectrometry.

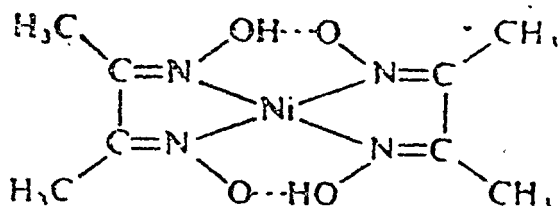
**Neutron Spectrum.** A plot or display of the number of neutrons at various energies, such as the neutrons emitted in a nuclear reaction, or the neutrons in a nuclear reactor.

**Nickel Accumulator.** The nickel accumulator uses the reaction



The reaction is carried out in an alkaline medium, usually potassium hydroxide with some lithium hydroxide. On charging, the  $\text{Fe(OH)}_2$  is reduced to Fe and the  $\text{Ni(OH)}_2$  oxidized to nickel(III) oxide. Its discharge-voltage is only about 1.2 V, and as compared with the lead accumulator it has a rather low current efficiency and a rather more expensive. It has some compensating advantages in lower weight and greater mechanical strength, for the electrode materials are compressed into perforated pockets of nickel-plated steel, and the accumulator can therefore withstand mechanical shocks and high rates of charge or discharge.

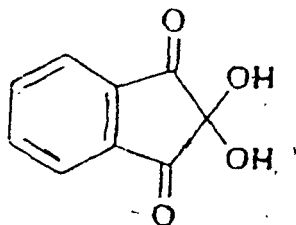
**Nickel Dimethylglyoxime.** The normal form in which nickel is weigh-



ed in analysis. There is metal-metal bonding in the solid. The red complex is precipitated from alkaline solution.

**Nicol.** An optical material (Iceland spar) that functions as a prism, separating light that rays pass through it into two portions, one of which is reflected away, and the other transmitted. The transmitted portion is called plane-polarized light.

**Ninhydrin, 1,2, 3-triketohydrindene Hydrate,  $C_9H_4O_3 \cdot H_2O$ .** Light



brown crystals, losing water at  $125-130^{\circ}\text{C}$ , m.p.  $242^{\circ}\text{C}$  (decomp.). It gives a blue colour on heating with proteins, peptides and amino-acids and is much used for their detection, particularly as a spray reagent in paper chromatography.

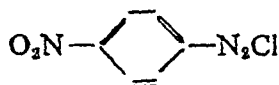
**Nitrates.** Salts of nitric acid,  $\text{HNO}_3$ . All metallic nitrates are soluble in water, some, *e.g.*  $\text{UO}_2(\text{NO}_3)_2$ , are readily extracted into organic solvents. Formed, generally as hydrates, from nitric acid and metal oxides, hydroxides and carbonates. Anhydrous nitrates, *e.g.*  $\text{Cu}(\text{NO}_3)_2$ , formed by dissolving Cu in liquid  $\text{N}_2\text{O}_4$  or reacting with  $\text{N}_2\text{O}_5$ , many adducts are formed with excess  $\text{N}_2\text{O}_4$ , they are soluble in organic solvents and are often volatile. Many nitrates are ionic but heavy metal nitrates and anhydrous nitrates have covalent bonded nitrate groups. On heating most nitrates decomposes to the metal oxide and  $\text{NO}_2$  and  $\text{O}_2$ , although  $\text{NaNO}_3$  and  $\text{KNO}_3$  give nitrites and oxygen and  $\text{NH}_4\text{NO}_3$  gives  $\text{N}_2\text{O}$  and  $\text{H}_2\text{O}$ . Nitrates may be tested for by the 'brown ring' test iron (II) sulphate is added to the cold solution to be tested, and concentrated sulphuric acid added down the side of the test tube; in the presence of nitrate a brown or black ring is formed at the junction of the two liquids. This test is unreliable in the presence of bromide or iodide (which also give coloured rings); a sounder test and estimation of nitrate is by reduction to

ammonia with Devarda's or Arnd's alloy and NaOH or by precipitating nitron nitrate. Nitric acid and the nitrates (particularly those of Na, K, Ca and  $\text{NH}_4$ ) are of great commercial importance; practically all modern explosives contain high proportions of ammonium nitrate or organic nitro-compounds. Nitrates are also employed as fertilizers.

**Nitrating Acid.** Generally a mixture of nitric and sulphuric acids used for commercial nitration, *e.g.* in the production of nitroglycerin.

**Nitration.** A reaction in which a nitro group ( $-\text{NO}_2$ ) replaces a hydrogen on a carbon atom by the use of nitric acid or mixed acid. An example is the nitration of cellulose to nitrocellulose. It is widely used in aromatic reactions to form such compounds as nitrobenzene, trinitrotoluene, nitroglycerin and other explosives. Aromatic nitrations are usually effected with mixed acid, a mixture of nitric and sulfuric acids, at 0 to  $120^\circ\text{C}$ . Aliphatic nitration is less common than aromatic, but propane can be nitrated under pressure to yield nitroparaffins.

**P-nitrobenzonediazonium Chloride Reagent.** Ammonium salts form



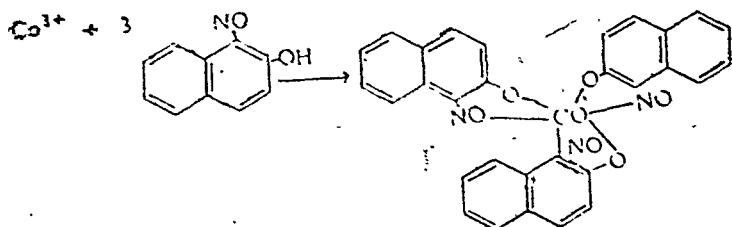
red zone around the CaO with the reagent.

**Test Place** a drop of the test solution (neutral or slightly acidic) on a spot plate, followed by 1 drop of the reagent and a fine granule of CaO between the two drops.

A red zone around the CaO indicates ammonium. The limit of identification being  $0.7 \mu\text{g NH}_4^+$ ; conc. limit, 1 in 75,000.

**$\alpha$ -nitroso  $\beta$ -naphthol.** This is mainly used to precipitate Co (III) in the presence of Nickel. It is a brown powder, insoluble in water and soluble in acetic acid. With Co(III), in acidic medium,

the reagent forms a reddish brown precipitate, with a composition  $\text{Co}(\text{C}_{10}\text{H}_6\text{O}_2\text{N}_3)_3$ . The complex can also be converted into  $\text{Co}_3\text{O}_4$  by ignition and weighed as such.

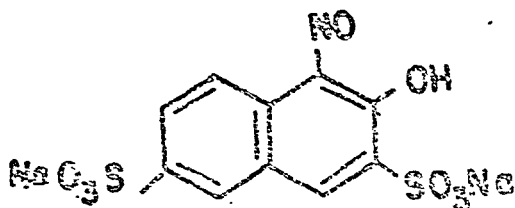


This reagent is also used to detect cobalt.

Test place 1 drop of the test solution on filter paper and add 1 drop of the reagent solution (0.1 g reagent in 20 mL water and 1 mL dil NaOH and diluting to 200 mL with water).

A pink ring indicates cobalt, the limit of identification being  $0.05 \mu\text{g Co}$ ; conc. limit, 1 in 1,000,000.

**Nitroso-r-salt Reagent.** Cobalt salts give deep red colour with the



reagent. The interference is due to Sn and Fe. The interference due to iron can be prevented by the addition of an alkali fluoride.

Test Place 1 drop of the neutral test solution (buffered with  $\text{CH}_3\text{COONa}$ ) on a spot plate, add 2-3 drops of the reagent solution (1% aqueous solution).

A red colour indicates cobalt, conc. limit. 1 in 500,000.

**Nitrogen Solutions.** Aqueous solutions of ammonium nitrate, ammonia, and/or urea. They are graded according to total nitrogen content and composition.

**Nitrogen Solution.** Mixture used to neutralize super-phosphate in fertilizer manufacture; consists of 60% ammonium nitrate, and the balance a 50% aqua ammonia solution.

**Nitrometer.** Glass apparatus used to collect and measure nitrogen and other gases evolved by a chemical reaction. Also known as azotometer.

**Nitron** (1,4-diphenyl-3,5-endo-anilino-4,5-dihydro-1,2,4-triazole)  
 $C_{20}H_{16}N_4$ .

Properties : Lemon-yellow, fine crystalline needles. Soluble in chloroform, acetone, and acetic acid ester; slightly soluble in ether and alcohol; insoluble in water.

Use: Reagent for detection of nitrate, perchlorate, boron, rhenium.

**Nomograph.** A chart in which a straight line either drawn or indicated by a ruler, intersects three scales at points that represent values that satisfy an equation.

**N Line.** One of the characteristic lines in an atom's x-ray spectrum, produced by excitation of an N electron.

**NMR.** Abbreviation for Nuclear Magnetic Resonance.

**Nonaqueous.** Pertaining to a liquid or solution containing no water.

**Noncrossing Rule.** The rule that when the potential energies of two electronic states of a diatomic molecule are plotted as a function of distance between the nuclei, the resulting curves do not cross, unless the states have different symmetry.

**Nonideal Solution** A solution whose behavior does not conform to that of an ideal solution; that is, the behavior is not predictable over a wide range of concentrations and temperatures by the use of Raoult's law.

**Nonlinear Molecule.** A branched-chain molecule, that is, one whose atoms do not all lie along a straight line. Also known as isomolecule.

**Nonlinear Spectroscopy.** The study of energy levels not normally accessible with optical spectroscopy, through the use of non-linear effects such as multiphoton absorption and ionization.

**Normal Bonded-phase Chromatography.** A technique of bonded-phase chromatography in which the stationary phase is polar and the mobile phase is non-polar.

**Normality.** Measure of the number of gram- equivalent weights of a compound per liter of solution. Abbreviated N.

**Normal Mass Shift.** The portion of the mass shift that corresponds to the variation of reduced mass, and is thus easily calculated for all transitions..

**Normal Salt.** A salt in which all of the acid hydrogen atoms have been replaced by a metal, or the hydroxide radicals of a base are replaced by an acid radical; for example,  $\text{Na}_2\text{CO}_3$ .

**Normal Solution.** A solution which contains 1 g equivalent of the substance in 1 litre of solution. A normal solution must have the equivalent referred to a specific reaction and this is often not done. A normal solution may be indicated by the letter N, thus, N-hydrochloric acid signifies a normal solution of hydrogen chloride (for titration with base).

**Normal State.** A term sometimes used for ground state.

**NQR Spectroscopy.** See nuclear quadrupole resonance.

**Nuclear Magnetic Moment.** The magnetic dipole moment of an atomic nucleus; a vector whose scalar product with the magnetic flux density gives the negative of the energy of interaction of a nucleus with a magnetic field.

**Nuclear Magnetic Resonance (NMR).** A type of radio-frequency spectroscopy, based on the magnetic field generated by the spinning of electrically charged atomic nuclei. This nuclear magnetic field is caused to interact with a very large (10,000-50,000 gauss) magnetic field of the instrument magnet. The magnetic properties of atomic nuclei are the spin number and

the magnetic moment. Hydrogen nuclei, fluorine, phosphorus, boron, nitrogen, carbon-13, and oxygen-17 have distinctive magnetic properties. The molecular or chemical environment of the nucleus produces characteristic shifts and fine structure in the NMR spectra. Because of its dependence on molecular structure, NMR has become a fundamental research tool for structure determinations in organic chemistry. Studies of hydrogen locations in crystal have been useful, as these cannot be determined directly by means of x-rays. NMR techniques have been applied to studies of electron densities and chemical bonding, the composition of mixtures, percentage purity determinations and elemental hydrogen analyses.

**Nuclear Magnetic Resonance Spectrometer.** A spectrometer in which nuclear magnetic resonance is used for the analysis of protons and nuclei and for the study of changes in chemical and physical quantities over wide frequency ranges.

**Nuclear Magneton.** A unit of magnetic dipole moment used to express magnetic moments of nuclei and baryons; equal to the electron charge times Planck's constant divided by the product of  $4\pi$ , the proton mass, and the speed of light.

**Nuclear Moment.** One of the various static electric or magnetic multipole moments of a nucleus.

**Nuclear Polarization.** For a nucleus in a mixed state, with spin  $I$  and probability  $p(I_z)$  that the  $I_z$  substate is populated, the polarization is sum over allowed values of  $I_z$  of  $I_z p(I_z)/I$ .

**Nuclear Quadrupole Moment.** The electric quadrupole moment of an atomic nucleus.

**Nuclear Quadrupole Resonance (NQR).** A spectroscopic technique related to nuclear magnetic resonance which utilizes the electric fields naturally present in crystals instead of a magnet. It is useful for studies of electrical field gradients around nuclei, chemical bonding, space groupings in crystals and molecular structure.



**Nuclear Radiation Spectroscopy.** Study of the distribution of energies or momenta of particles emitted by nuclei.

**Nuclear Reaction Spectrometry.** A method of determining the concentration of a given element as a function of depth beneath the surface of a sample, by measuring the yield of characteristic gamma rays from a resonance reaction occurring when the surface is bombarded by a beam of ions. Abbreviated NRS.

### **Nuclear Resonance**

1. An unstable excited state formed in the collision of a nucleus and a bombarding particle, and associated with a peak in a plot of cross section versus energy.
2. The absorption of energy by nuclei from radio-frequency fields at certain frequencies when these nuclei are also subjected to certain types of static fields, as in magnetic resonance and nuclear quadrupole resonance.

### **Nuclear Spectrum**

1. The relative number of particles emitted by atomic nuclei as a function of energy or momenta of the separticles.
2. The graphical display of data from devices used to measure these quantities.

**Nuclear Spin.** The total angular momentum of an atomic nucleus, resulting from the coupled spin and orbital angular momenta of its constituent nuclei. Also known as nuclear angular momentum. Symbolized  $I$ .

**Nuclear Zeeman Effect.** A splitting of atomic spectral lines resulting from the interaction of the magnetic moment of the nucleus with an applied magnetic field.

**Nylander Reagent.** A solution Rochelle salt (potassium sodium tartrate), potassium or sodium hydroxide, and bismuth subnitrate in water; used to test for sugar in urine.

# O

**Obermayer's Reagent.** A 0.4% solution of ferric chloride in concentrated hydrochloric acid; used to test for indican in urine, with a pale-blue or deep-violet color indicating positive.

**Oleum.** The Latin word for oil, applied to fuming sulfuric acid (q.v.); (sulfuric acid was originally called oil of vitriol).

**Open-circuit Potential.** The steady-state or equilibrium potential of an electrode in absence of external current flow to or from the electrode.

**Opacity.** The optical density of a material, usually a pigment; the opposite of transparency. A colorant or paint of high opacity is said to have good hiding power or covering power, by which is meant its ability to conceal another tint or shade over which it is applied. Apparatus for measuring opacity is available.

**Optical Anomaly.** The phenomenon in which an organic compound has a molar refraction which does not agree with the value calculated from the equivalents of atoms and other structural units composing it.

**Optical Crystals.** A comparatively large crystal, either natural or synthetic, used for infrared and ultraviolet optics, piezoelectric effects, and short wave radiation detection. Examples are sodium chloride, potassium iodide, silver chloride, calcium fluoride, and (for scintillation counters) such organic materials as anthracene, naphthalene, stilbene, and terphenyl.

**Optical Exaltation.** Optical anomaly in which the observed molar refraction exceeds the calculated one; most cases of optical anomaly are in this category.

**Optical Microscope (light microscope).** A magnifying lens system that utilizes light in the visible wavelength range of the

electromagnetic spectrum (about 5000 Angstrom units). A convex glass lens bends or focuses light waves because of the difference in density between glass and air. Invented in 1959 by the Janssen brothers and later improved by van Leeuwenhoek, the compound microscope has three lenses: a condenser lens, which concentrates the incident light; an objective lens, which gives an enlarged reverse image of the specimen; and a projector lens, which further enlarges the image and returns it to normal position. Its maximum resolving power is approximately 0.5 micron, compared with 100 microns for the human eye. The compound microscope is particularly useful in studying bacteria and other microorganisms in their natural state without interfering with their behavior. It has been of untold benefit to biologists and bacteriologists, and also has innumerable uses in chemical and metallurgical research, as well as in forensic chemistry.

**Optical Model.** See cloudy crystal-ball model.

**Optical Monochromator.** A monochromator used to observe the intensity of radiation at wavelengths in the visible, infrared, or ultraviolet regions.

**Optical Null Method.** In infrared spectrometry, the adjustment of a reference beam's energy transmission to match that of a beam that has been passed through a same being analyzed.

**Optical Rotation.** The change of direction of the plane of polarized light to either the right or the left as it passes through a molecule containing one or more asymmetric carbon atoms, *e.g.*, sugars. The direction of rotation, if to the right, is indicated by either a plus sign (+) or an italic *d*; if to the left, by a minus sign (—) or an italic *l*. Molecules having a right-handed configuration (D) usually are dextrorotatory, D(+), though they may be levorotatory, D(—); those having a left-handed configuration (L) are usually levorotary, L(—), but may be dextrorotatory, L(+). Compounds having this property are said to be optically active and are isomeric. The amount of rotation varies with

the compound, but is the same for any two isomers, though in opposite directions.

**Optical Spectra.** Electromagnetic spectra for wavelengths in the ultraviolet, visible and infrared regions, ranging from about 10 nanometers to 1 millimeter, associated with excitations of valence electrons of atoms and molecules, and vibrations and rotations of molecules.

**Optical Spectrograph.** An optical spectroscope provided with a photographic camera or other device for recording the spectrum made by the spectroscope.

**Optical Spectrometer.** An optical spectroscope that is provided with a calibrated scale either for measurement of wavelength or for measurement of refractive indices of transparent prism materials.

**Optical Spectroscope.** An optical instrument, consisting of a slit; collimator lens, prism or grating, and a telescope or objective lens, which produces an optical spectrum arising from emission or absorption of radiant energy by a substance, for visual observation.

**Optical Spectroscope.** The production, measurement, and interpretation of optical spectra arising from either emission or absorption of radiant energy by various substances.

**Optoacoustic Detection Method.** A method of detecting trace impurities in a gas, in which the absorption of a sample of the gas at various light frequencies is measured by directing a periodically interrupted laser beam through the sample in a spectrophone and measuring the sound generated by the optoacoustic effect at the frequency of interruption of the beam.

**Orange Spectrometer.** A type of beta-ray spectrometer that consists of a number of modified double-focusing spectrometers employing a common source and a common detector, and has exceptionally high transmission.

**Organic Solvent.** Liquid organic compound with the power to dissolve solids, gases, or liquids (miscibility); examples are methanol (methyl alcohol),  $\text{CH}_3\text{OH}$ , and benzene,  $\text{C}_6\text{H}_6$ .

**Organometallic Compound.** Molecules containing carbon-metal linkage; a compound containing an alkyl or aryl radical bonded to a metal, such as tetraethyllead,  $\text{Pb}(\text{C}_2\text{H}_5)_4$ .

**Orsat Analyzer.** Gas analysis apparatus in which various gases are absorbed selectively (volumetric basis) by passing them through a series of preselected solvents.

**Orsat Gas-analysis Apparatus.** Generally portable apparatus with a gas-measuring burette from which the gas may be transferred to various absorption pipettes. Often used for flue-gas analysis with absorption by :

- (1)  $\text{KOH}$  solution for  $\text{CO}_2$ ;
- (2) alkaline pyrogallol for  $\text{O}_2$ ;
- (3)  $\text{CuCl}/\text{HCl}$  for  $\text{CO}$ .

$\text{H}_2$ ,  $\text{CH}_4$  and other combustible gases are determined by combustion by sparking and estimation of the resultant  $\text{CO}_2$ .

**Oscillator Strength.** A quantum-mechanical analog of the number of dispersion electrons having a given natural frequency in an atom, used in an equation for the absorption coefficient of a spectral line; it need not be a whole number. Also known as  $f$  value; Ladenburg  $f$  value.

**Oscillatory Reaction.** A chemical reaction in which a variable of a chemical system exhibits regular periodic changes in time or in space.

**Oscillographic Polarography.** A type of voltammetry using a dropping mercury electrode with oscillographic scanning of the applied potential; used to measure the concentration of electroactive species in solutions.

**Oscillometric Titration.** Radio-frequency technique used for conductometric and dielectrometric titrations; the changes in conductance or dielectric properties changes the solution

capacity and thus the frequency of the connected oscillator circuit.

**Oscillometry.** Electrode measurement of oscillation-frequency changes to detect the progress of a titration of electrolytic solutions.

**Osmic Acid Anhydride  $\text{OsO}_4$ .** Poisonous yellow crystals with disagreeable odor; melts at  $40^\circ\text{C}$ ; soluble in water, alcohol, and ether; used in medicine, photography, and catalysis. Also known as osmium oxide; osmium tetroxide.

**Osmolality.** The molality of an ideal solution of a nondissociating substance that exerts the same osmotic pressure as the solution being considered.

**Osmolality.** The molality of an ideal solution of a nondissociating substance that exerts the same osmotic pressure as the solution being considered.

### Osmole

1. The unit of osmolarity equal to the osmolarity of a solution that exerts an osmotic pressure equal to that of an ideal solution of a nondissociating substance that has a concentration of 1 mole of solute per litre of solution.
2. The unit of osmolality equal to the osmolality of a solution that exerts an osmotic pressure equal to that of an ideal solution of a nondissociating substance that has a concentration of 1 mole of solute per kilogram of solvent.

**Osmometer.** A device for measuring molecular weights by measuring the osmotic pressure exerted by solvent molecules diffusing through a semipermeable membrane.

**Osmosis.** The transport of a solvent through a semipermeable membrane separating two solutions of different solute concentration, from the solution that is dilute in solute to the solution that is concentrated.

### Osmotic Pressure

1. The applied pressure required to prevent the flow of a solvent across a membrane which offers no obstruction to passage of the solvent, but does not allow passage of the solute, and which separates a solution from the pure solvent.
2. The applied pressure required to prevent passage of a solvent across a membrane which separates solutions of different concentration, and which allows passage of the solute, but may also allow limited passage of the solvent. Also known as osmotic gradient.

**Ostwald Dilution Law.** The law that for a sufficiently dilute solution of univalent electrolyte, the dissociation constant approximates  $a^2c(1-a)$ , where  $c$  is the concentration of electrolyte and  $a$  is the degree of dissociation.

**Oswald Diagram.** Diagram used in fuel Orsat analyses by plotting percent by volume  $\text{CO}_2$  maximum in the fuel (ordinate) versus percent by volume  $\text{O}_2$  in air (abscissa);  $\text{O}_2$  and  $\text{CO}_2$  Orsat readings should fall on a line connecting these maximum values if the analysis is proceeding properly.

**Oudemans Law.** The law that the molecular rotations of the various salts of an acid or base tend toward an identical limiting value as the concentration of the solution is reduced to zero.

**Overall Plate Efficiency.** For a specified liquid-mixture separation in a fractionation (or distillation) tower, the ratio of actual to theoretical plates (or trays) required.

**Overall Stability Constant.** Reaction equilibrium constant for the reaction forming soluble complexes during compleximetric titration.

**Overcritical Electric Field.** An electric field so strong that an electro-position pair is created spontaneously, quantum, electrodynamics predicts that this will happen near a nucleus having more than approximately 173 protons.

**Overgrowth.** A crystal growth in optical and crystallographic continuity around another crystal of different composition.

**Overhauser Effect.** The effect whereby, if a radio frequency field is applied to a substance in an external magnetic field, whose nuclei have spin  $\frac{1}{2}$  and which has unpaired electrons, at the electron spin resonance frequency, the resulting polarization of the nuclei is as great as if the nuclei had the much larger electron magnetic moment.

**Overpoint.** The initial boiling point in a distillation process; specifically, the temperature at which the first drop falls from the tip of the condenser into the condensate flask.

**Overpotential.** See overvoltage.

**Overtone Band.** The spectral band associated with transitions of a molecule in which the vibrational quantum number changes by 2 or more.

**Overvoltage.** The difference between electrode potential under electrolysis conditions and the thermodynamic value of the electrode potential in the absence of electrolysis for the same experimental conditions. Also known as overpotential.

**Oxalic Acid  $\text{HOOC}\cdot\text{COOH}\cdot 2\text{H}_2\text{O}$ .** Poisonous, transparent, colorless crystals melting at  $187^\circ\text{C}$ ; soluble in water, alcohol, and ether; used as a chemical intermediate and a bleach, and in polishes and rust removers.

## Oxidation

1. A chemical reaction that increase the oxygen content of a compound.
2. A chemical reaction in which a compound or radical loses electrons, that is in which the positive valence is increased.

## Oxidation Number

1. Numerical charge on the ions of an element.
2. See oxidation state.



**Oxidation Potential.** The difference in potential between an atom or ion and the state in which an electron has been removed to an infinite distance from this atom or ion.

**Oxidation-reduction Indicator.** A substance that has a color in the oxidized form different from that of the reduced form, and can be reversibly oxidized and reduced. Thus if diphenylamine is present in a ferrous sulfate solution to which potassium dichromate is added, a violet color appears with the first drop of excess dichromate.

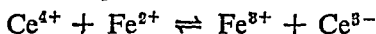
**Oxidation-reduction Reaction.** An oxidizing chemical change, where an element's positive valence is increased (electron loss), accompanied by a simultaneous reduction of an associated element (electron gain).

**Oxidation-reduction Titrations** Oxidation is a process in which a substance loses electrons and reduction is the reverse process of oxidation in which the substance gains electrons. For example during the reaction of Zn and  $\text{Cu}^{2+}$ ,



Zinc is getting oxidised and copper ion is reduced to metallic copper.

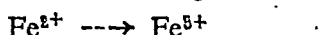
The substance oxidising other substance is called as oxidant or oxidising agent and during the process of oxidation, the oxidising agent gets itself reduced. Similarly a reducing agent or reductant is getting oxidised during reduction. Reaction of  $\text{Ce}^{4+}$  and  $\text{Fe}^{2+}$  is represented as



Many redox titrations are carried out using visual indicators which due to colour change can detect and point. There are three types of redox indicators.

**Oxidation State.** The number of electrons to be added (or subtracted) from an atom in a combined state to convert it to elemental form. Also known as oxidation number.

**Oxidizing Agent.** A material which brings about oxidation and in the process is itself reduced. E.  $\text{MnO}_4^-$  in acid oxidizes



and is itself reduced to  $\text{Mn}^{2+}$ .

**Oxidizing Flame.** A flame, or the portion of it, that contains an excess of oxygen.

**Oxime.** Compound containing the  $\text{CH}(:\text{NOH})$  radical; condensation product of hydroxylamine with aldehydes or ketones.

**Oxine**  $\text{C}_9\text{H}_6\text{NOH}$ . White powder that darkens when exposed to light; slightly soluble in water, dissolves in ethanol, acetone, and benzene; used to prepare fungicides and to separate metals by precipitations. Also known as 8-hydroxyquinoline; oxyquinoline; 8-quinolinol.

**Oxygen Absorbent.** Any material that will absorb (dissolve) oxygen into its body without reacting with it.

**Oxygen-flask Method.** Technique to determine the presence of combustible elements; the sample is burned with oxygen in a closed flask, and combustion products are absorbed in water of dilute alkali with subsequent analysis of the solution.

**Oxyhydrogen Flame.** A flame obtained from the combustion of a mixture of oxygen and hydrogen.

### Ozonolysis

- (1) Oxidation of an organic material by means of ozone, *i.e.*, tall oil, oleic acid, safflower oil, cyclic olefins; carbon treatment; paracetic acid production.
- (2) The use of ozone as a tool in analytical chemistry to locate double bonds in organic compounds, and a similar use in synthetic organic chemistry for preparing new compounds. Under proper conditions, ozone attaches itself at the double bond of an unsaturated compound to form an ozonide. Since many ozonides are explosive, it is customary to decompose them in solution and deal with the final product.

## P

**Paar Turbidimeter.** A visual-extinction device for measurement of solution turbidity; the length of the column of liquid suspension is adjusted until the light filament can no longer be seen.

**Packed Bed.** A fixed layer of small particles or objects arranged in a vessel to promote intimate contact between gases, vapors, liquids, solids or various combinations thereof; used in catalysis, ion exchange, sand filtration, distillation, absorption, and mixing.

**Packed Column, Packed Tower.** One of the two principal types of plant used for gas-liquid contacting. It consists of a long vertical column filled with a packing material over which the liquid flowing down the column, solvent in the case of gas absorption or reflux in the case of distillation, can spread itself, thus providing a large area for contact between phases. For efficient operation this liquid must be spread evenly over the top of the packing, this being done by a distributor. The greater the packed height of the column the greater the path length over which transfer of material between phases can occur, and thus the degree of separation or absorption that such a unit can achieve is directly related to this height.

Packed columns are widely used for gas absorption and for small-scale industrial distillation operations. They provide a low resistance to the flow of gas or vapour, simple in construction and can be readily made from corrosion-resistant materials. Distribution of liquid is a problem in large diameter units. Packed columns are also used for liquid-liquid extraction.

**Packed Tower.** A fractionating or absorber tower filled with small objects (packing) to bring about intimate contact between rising fluid (vapor or liquid) and falling liquid.

**Packed Tube.** A pipe or tube filled with high-heat-capacity granular material; used to heat gases when tubes are externally heated.

**Packings. Column Packings, Tower Packings.** Wood metal and plastic grids are used in absorption and cooling towers. Raschig rings, cylinders of metal, ceramic or glass with length equal to diameter, are used for packings in both distillation and absorption columns. Saddles, ceramic pieces in the shape of a saddle, are more efficient than Raschig rings, though more expensive. High efficiency packings are used in distillation columns for difficult separations where it is necessary to obtain a large number of theoretical plates in a comparatively small packed height. They generally consist of metal in the form of gauze or wire mesh.

Paper Chromatography has found very wide applications in quantitative analysis of metal ions and their separation from a mixture. In paper chromatography, a filter paper is acting as the stationary phase in which a solution of the mixture to be separated is placed. Suitable solvent which dissolves the solutes is acting as the mobile phase. The separation of components represent is based on the absorption and capillary action of the filter paper which act as a stationary phase.

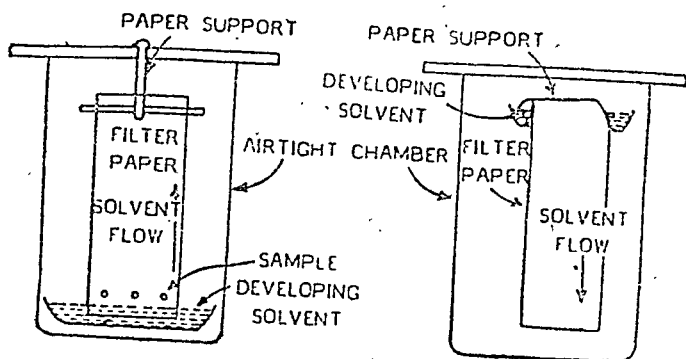
Paper Chromatography is divided into two types (1) Ascending paper chromatography, (2) Descending paper chromatography. In ascending method, the solvent molecules moves up the filter paper, and in descending method, the solvent moves down the filter paper. In paper chromatography a filter paper of 15 cm length and 3—4 cm breadth is taken and in which a line is drawn at a distance from the end. This line is called as starting. To this point, the solution of a mixture of cations is added in small quantities (2 ml) and the solution is allowed to evaporate. A deposit of solutes is felt on the filter paper. The filter paper is then suspended in a glass jar containing suitable solvent, such that the solvent moves in the filter paper from the start line, allowing the solute to dissolve in the

solvent and move to different distances from the start line depending on their adsorption with the stationary phase. Depending on the movement of solvent, the paper chromatography is called as ascending or descending type. The progress of the solvent front as it flows through the paper is noted before the filter paper is allowed to dry. If colourless substances are present in a solution, then the different solutes can be identified by examining the filter paper. The position of the solute and the solvent front are marked on the filter paper. If  $dA$  and  $dB$  are the distances travelled by the solvent from the startline,  $dA$  and  $dB$  are the distances travelled by the solutes A and B, then their  $R_f$  values are given by,

$$(R_f)_A = \frac{dA}{DS} ; (R_f)_B = \frac{dB}{dS}$$

$$R_f = \frac{\text{Distance travelled by the solute component}}{\text{Distance travelled by the solvent}}$$

The  $R_f$  values are characteristic of each and every substance and quantitative separation is possible.



**Papanicolaou's Stains.** A group of stains used on exfoliated cells, particularly those from the vagina, for examination and diagnosis.

**Paper.** A semisynthetic product made by chemically processing cellulosic fibres. Wide varieties of sources have been used for speciality papers (flax, bagasse, esparto, straw, papyrus, bam-

boo, jute, and others), but by far the largest quantity is made from softwoods (coniferous trees), such as spruce, hemlock, pine, etc.; some is also made from such hardwoods as poplar, oak, etc., as well as from synthetic fibres. Papermaking technology involves the following basic steps :

- (1) chipping or other subdivision of the logs (see ground-wood);
- (2) manufacture of chemical or semichemical pulp by digestion in acidic or alkaline solutions, which separates the cellulose from the lignin (see pulp, paper);
- (3) beating the pulp to break down the fibres and permit proper bonding when the sheet is formed;
- (4) addition of starches, resins, clays, and pigments to the liquid stock (or "furnish");
- (5) formation of the sheet continuously on a fourdrinier machine, where the water is screened out and the sheet dried by passing over a series of heated drums;
- (6) high-speed calendering for brightness and finish;
- (7) coating, either by machine application or (for heavy finishes) by brushes.

**Paper Chromatography. (PC).** A microtype of chromatography (q.v.). A drop of the liquid to be investigated is placed near one end of a strip of paper. This end is immersed in solvent, which travels down the paper and distributes the materials present in the original drop selectively. Comparison with known substances makes identification possible.

**Paper Electrochromatography.** Variation of paper electrophoresis in which the electrolyte-impregnated absorbent paper is suspended vertically and the electrodes are connected to the sides of paper, producing a current at right angles to the downward movement of the unknown sample.

**Paper Electrophoresis.** A variation of paper chromatography in which an electric current is applied to the ends of the electrolyte-

impregnated absorbent paper, thus moving chargeable molecules of the unknown sample toward the appropriate electrode.

**Paper-tape Chemical Analyzer.** Chemically treated paper tape that is continuously unreeled, exposed to the sample, and viewed by a phototube to measure the color change that is empirically related to changes in the sample's chemical composition.

**Parachor.** The existence of intermolecular attractive forces in liquids does not permit the use of molecular volumes for comparisons of molecular dimensions. The parachor  $p$ , where

$$p = \gamma^{\frac{1}{2}} \frac{M}{D - d}$$

$\gamma$  is the surface tension,  $M$  the molecular weight and  $D$  and  $d$  the densities of the liquid and vapour respectively, is an empirical measure of molecular volume and was widely used to determine the constitution of organic and inorganic compounds.

**Paramagnetic Analytical Methods.** Analysis of fluid mixtures by measurement of the paramagnetic (versus diamagnetic) susceptibilities of materials when exposed to a magnetic field.

**Paramagnetic Spectra.** Spectra associated with the coupling of the electronic magnetic moments of atoms or ions in paramagnetic substances, or in paramagnetic centers of diamagnetic substances, to the surrounding liquid or crystal environment, generally at microwave frequencies.

**Parr Formula.** A formula used to determine the mineral matter of a coal from the ash left when the coal is burned.

**Partial Condenser.** The type of condenser is sometimes used on distillation columns where the overhead product is a mixture of vapours and condensation therefore occurs over a temperature range. The vapour is partially condensed by heat exchange with another process stream, and the remainder is condensed in a final condenser using cooling water. The advantage of this arrangement is that some of the heat in the vapour stream is utilized, and at the same time the vapour itself is enriched in the more volatile components. The partial condenser is sometimes called a dephlegmator.

**Partial Molar Volume.** That portion of the volume of a solution or mixture related to the molar content of one of the components within the solution or mixture.

**Particle Counting.** Microscopic or photomicrographic technique for the visual counting of the numbers of particles in a known quantity of a solid-liquid suspension.

**Particle Electrophoresis.** Electrophoresis in which the particles undergoing analysis are of sufficient size to be viewed either with the naked eye or with the assistance of an optical microscope.

**Particle-induced X-ray Emission.** A method of trace analysis in which a beam of ions is directed at a thin foil on which the sample to be analyzed has been deposited and the energy spectrum of the resulting x-rays is measured.

**Particle-scattering Factor.** Factor in light-scattering equations used to compensate for the loss in scattered light intensity caused by destructive interference during the analysis of macromolecular compounds.

**Particle-thickness Technique.** Microscopic technique for visual measurement of the thickness of a fine particle (in the 3—100 micrometer range).

**Partition Chromatography.** Chromatographic procedure in which the stationary phase is a high-boiling liquid spread as a thin film on an inert support, and the mobile phase is a vaporous mixture of the components to be separated in an inert carrier gas.

**Partition Coefficient.** In the equilibrium distribution of a solute between two liquid phases, the constant ratio of the solute's concentration in the upper phase to its concentration in the lower phase. Symbolized  $K$ .

**Parylene.** Polyparaxylylene, used in ultrathin plastic films for capacitor dielectrics, and as a pore-free coating.



**Pascal Rules.** Rules which give the diamagnetic susceptibility of a complex molecule in terms of the sum of the susceptibilities of its constituent atoms, and a correction factor which depends on the type of bonds linking the atoms.

**Paschen-back Effect.** An effect on spectral lines obtained when the light source is placed in a very strong magnetic field; the anomalous Zeeman effect obtained with weaker fields changes over to what is, in a first approximation, the normal Zeeman effect.

**Paschen-runge Mounting.** A diffraction grating mounting in which the slit and grating are fixed, and photographic plates are clamped to a fixed track running along the corresponding Rowland circle.

**Paschen Series.** A series of lines in the infrared spectrum of atomic hydrogen whose wave numbers are given by  $R_H[(1/9)-(1/n^2)]$ , where  $R_H$  is the Rydberg constant for hydrogen, and  $n$  is any integer greater than 3.

**Passivation Potential.** The potential corresponding to the critical anodic current density of an electrode which behaves in an active-passive manner.

**Pasteurization.** Heat treatment of milk, fruit juices, canned meats, egg products, etc., for the purpose of killing or inactivating disease-causing organisms. For milk, the minimum exposure is 62°C for 30 minutes, or 72°C for 15 seconds, the latter being called flash pasteurization. Though this treatment kills all pathogenic bacteria and also inactivates enzymes which cause deterioration of the milk, the shelf-life is limited; to prolong storage life temperatures of 80 to 88°C for 20 to 40 seconds must be used. Complete sterilization (q.v.) requires ultra-high pasteurization at from 94°C for 3 seconds to 150°C for 1 second; in-can heating at 116°C for 12 minutes and 130°C for 3 minutes is also employed for maximum stability and long storage life. Some meat products are pasteurized by alpha-radiation.

**Pasteur's Salt Solution.** Laboratory reagent consisting of potassium phosphate and calcium phosphate, magnesium sulfate, and ammonium tartrate in distilled water.

**Pauli G-permanence Rule.** For given  $L$ ,  $S$ , and  $M_J$  in LS coupling, the sum, over  $J$ , of the weak-field  $g$ -factors is equal to the sum of the strong-field factors.

**Pauli G-sum Rule.** For all the states arising from a given electron configuration, the sum of the  $g$ -factors for levels with the same  $J$  value is a constant, independent of the coupling scheme.

**Pavy's Solution.** Laboratory reagent used to determine the concentration of sugars in solution by color titration; contains copper sulfate, sodium potassium tartrate, sodium hydroxides and ammonia in water solution.

**Peak Enthalpimetry.** A thermochemical analytical procedure applicable to bio-chemical and chemical analyses; the salient feature is rapid mixing of a reagent stream with an isothermal solvent stream into which discrete samples are intermittently injected; peak enthalpograms result which exhibit the response characteristics of genuine differential detectors.

**Peak Width.** In a gas chromatogram (plot of eluent rise and fall versus time), the width of the base (time duration) of a symmetrical peak (rise and fall) of eluent.

**Pebble Heater.** Gas-heating device (for air, hydrogen, methane, and steam) in which heat is transferred to the gas via a counter-current movement of pre-heated pebbles.

**Peclet Number.** Dimensionless group used to determine the chemical reaction similitude for the scale-up from pilot-plant data to commercial-sized units; incorporates heat capacity, density, fluid velocity, and other pertinent physical parameters.

**Pellet Cooler.** Gas-cooled, gravity-bed device for the cooling and drying of extruded pellets and briquets.

**Pellicular Resins.** Glass spheres coated with a thin layer of ion-exchange resin, used in liquid chromatography.

**Penetration Index.** An indication of the temperature susceptibility (*i.e.* change of viscosity with temperature) of bitumen expressed by a single figure derived from the Ring and Ball softening point and the penetration at 25°C.

**Penetrometer.** An instrument for carrying out penetration tests for the determination of the hardness of certain solids such as asphaltic bitumen, paraffin wax or grease.

**Pensky-martens Closed Tester.** Device to determine the ASTM flash point of fuel oils and cutback asphalts and other viscous materials and suspensions of solids.

**Peptization.** Stabilization of hydrophobic colloidal sols by addition of electrolytes, which provide the necessary electric double layer of ionic charges around each particle. Such electrolytes are known as peptizing agents. The ions of the electrolyte are strongly adsorbed on the particle surfaces. Stable sols of non-ionizing substances acquire a charge in contact with water by preferential adsorption of the hydroxyl ions, which may be considered peptizing agents. The term is also loosely applied to the softening or liquefaction of one substance by trace quantities of another, analogous to the digestion of a protein by an enzyme (pepsin).

**Peracetic Acid  $\text{CH}_3\text{COOOH}$ .** A toxic, colorless liquid with strong aroma; boils at 105°C explodes at 110°C; miscible with water, alcohol, glycerin, and ether, used as an oxidizer, bleach, catalyst, bactericide, fungicide, epoxy-resin precursor, and chemical intermediate. Also known as peroxyacetic acid.

**Perbenzoic Acid  $\text{C}_6\text{H}_5\text{CO}_2\text{OH}$ .** A crystalline compound forming leaflets from benzene solution, melting at 41–45°C, freely soluble in organic solvents; used, in analysis of unsaturated compounds and to change ethylinic compounds into oxides. Also known as benzylhydroperoxide; peroxybenzoic acid.

**Perchloric Acid  $\text{HClO}_4$**  Strongly oxidizing, corrosive colorless, hygroscopic liquid; boiling at 16°C (8 mmHg, or 1067 newtons per square meter); soluble in water unstable in pure form, but

stable when diluted in water, used in medicine, electrolytic baths, electropolishing, explosives and analytical chemistry, and as a chemical intermediate. Also known as Fraude's reagent.

**Percolation Filtration.** A continuous petroleum-refinery process in which lubrication oils and waxes are percolated through a clay bed to improve color, odor, and stability.

**Perforated-pipe Distributor.** Liquid distribution device consisting of a length of piping or tubing with holes at spaced intervals along the length; used in spray columns, liquid-vapor contactors, and spray driers. Also known as sparger.

**Perforated Plate.** Plate with series of holes used to control fluid distribution as in a perforated-plate (distillation) column.

**Perforated-plate Column.** Distillation column in which vapor-liquid contact is provided by perforated plates instead of bubble-cap trays.

**Perforated-plate Distributor**

1. A perforated plate or screen used to even out liquid-flow fluctuations through flow channels.
2. A perforated plate as used in a distillation column or liquid-liquid extraction column.

**Perforated-plate Extractor.** A liquid-liquid extraction vessel in which perforated plates are used to bring about contact between the two or more liquid phases.

**Periodic Acid  $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ .** Water-and alcohol-soluble white crystals; loses water at  $100^\circ\text{C}$ ; used as an oxidant.

**Peritectic.** A type of solid-liquid phase equilibrium system, commonly found with binary alloys, in which the two components form limited ranges of solid solution in each other, although they are completely miscible in the liquid state. A peritectic system differs from a eutectic system in that the former shows no minimum in the freezing-point composition curve.

**Permanganate.** A purple salt of permanganic acid containing the  $\text{MnO}_4^-$  radical; used as an oxidizing agent and a disinfectant.

**Permanganate Titrations.** On account of its intense colour and easy purification, potassium permanganate is an important volumetric oxidizing agent which requires no indicator even in 0.01 M-solution. When used, as in most estimations, in presence of sulphuric acid, it is reduced to  $\text{Mn}^{2+}$  (5 electrons). Solutions are standardized after having been boiled (or left to stand for some days) and then filtered. The best standards are sodium oxalate and pure (electrolytic) Fe; crystallized oxalic acid and  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  are also frequently used but are less reliable. The solution may be used for the direct titration of  $\text{Fe}^{2+}$ ,  $\text{H}_2\text{O}_2$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  oxalate, suitable back titrations enable it to be used for the estimation of a great variety of oxidizing and reducing agents. In the titration of  $\text{Fe}^{2+}$ ,  $\text{Cl}^-$  interferes but titration can be carried out in presence of an excess of manganese(II) sulphate. In some estimations permanganate is used in almost neutral solution, when hydrated manganese dioxide (or manganate(IV) is formed. An important instance of this procedure is the determination of Mn(II) the Volhard method); the titration is carried out in the presence of a  $\text{Zn}^{2+}$  salt and suspended  $\text{ZnO}$ .

**Permanganic Acid  $\text{HMnO}_4$**  An unstable acid that exists only in dilute solutions; decomposes to manganese dioxide and oxygen.

**Permeametry.** Determination of the average size of fine particles in a fluid (gas or liquid) by passing the mixture through a powder bed of known dimensions and recording the pressure drop and flow rate through the bed.

**Permeation.** The movement of atoms, molecules, or ions into or through a porous or permeable substance (such as zeolite or a membrane).

**Permeator.** A membrane assembly that performs an ion-exchange function, for example, desalting in a membrane water-desalting process.

**Permselective Membrane.** An ion exchange material that allows ions of one electrical sign to enter and pass through.

**Peroxide Number.** Measure of millimoles of peroxide (or milliequivalents of oxygen) taken up by 1000 grams of fat or oil; used to measure rancidity. Also known as peroxide value.

**Persulfuric Acid  $\text{H}_2\text{S}_2\text{O}_8$ .** Acid formed in lead-cell batteries by electrolyzing sulfuric acid; strong oxidizing agent.

**Petri Dish.** A small, concave glass plate having an easily removable cover, used for the culture of bacteria. Named after its inventor, a German biologist.

### Petrochemistry

1. An aspect of geochemistry that deals with the study of the chemical composition of rocks.
2. The chemistry and reactions of materials derived from petroleum, natural gas or asphalt deposits.

**Petroleum Ether.** This term is used synonymously with petroleum naphtha. It is also sometimes used as a synonym for ligroin or petroleum spirits. It is technically a misnomer, for it is not an ether in the chemical sense.

**Pfeiffer Effect.** The change in rotation of a solution of an optically active substance on the addition of a racemic mixture of an asymmetric compound.

**Rydberg Series.** A series of lines in the infrared spectrum of atomic hydrogen whose wave numbers are given by  $R_H[(1/n_1^2) - (1/n_2^2)]$ , where  $R_H$  is the Rydberg constant for hydrogen, and  $n$  is any integer greater than 5.

**pH.** A term used to describe the hydrogen-ion activity of a system; it is equal to  $-\log a_{H^+}$ ; here  $a_{H^+}$  is the activity of the hydrogen ion; in dilute solution, activity is essentially equal to concentration and pH is defined as  $-\log_{10} [H^+]$ , where  $[H^+]$  is hydrogen-ion concentration in moles per litre; a solution of pH 0 to 7 is acid, pH of 7 is neutral, pH over 7 to 14 is alkaline.

**Phase Diagram.** A graphical representation of the equilibrium relationships between phases (such as vapor-liquid, liquid-solid) of a chemical compound, mixture of compounds, or solution.

**Phase Equilibria.** The equilibrium relationships between phases (such as vapor, liquid, solid) of a chemical compound or mixture under various conditions of temperature, pressure, and composition.

**Phase Solubility.** The different solubilities of a sample's solid constituents (phase) in a selected solvent.

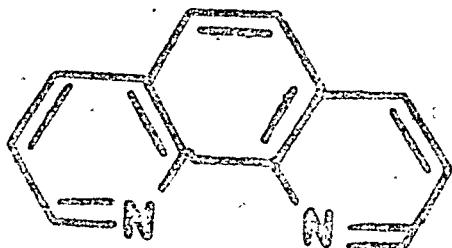
**Phase-solubility Analysis.** Solvent technique used to determine the amount and number of components in a solid substance; the weight of sample added to the solvent is plotted against the weight of sample dissolved, with breakpoints in the curve occurring with each progressive saturation of the solvent with respect to each of the components; can be combined with extraction and recrystallization procedures.

**Phase Titration.** Analysis of a binary mixture of miscible liquids by titrating with a third liquid that is miscible with only one of the components, using the ternary phase diagram to determine the end point.

**pH Electrode.** Membrane-type glass electrode used as the hydrogen-ion sensor of most pH meters; the pH-response electrode surface is a thin membrane made of a special glass.

**Phenanthroline Indicator.** A sensitive, red-colored specific reagent for iron. Also known as bathophenanthroline; 4, 7-diphenyl-1, 10-phenanthroline.

O-Phenanthroline Reagent.



Iron(II) salts give red colour with the reagent in fainty acidic solution. Reduce iron(III) to iron(II) as above.

Test Place 1 drop of reduced iron(III) on the spot plate and add 1 drop of the reagent solution (0.1% aqueous solution).

A red colour indicates iron, the conc. limit, 1 in 1,50,000.

**Phenol Coefficient.** In determining the effectiveness of a disinfectant using phenol as a standard of comparison, the phenol coefficient is a value obtained by dividing the highest dilution of the test disinfectant by the highest dilution of phenol that sterilizes a given culture of bacteria under standard conditions of time and temperature.

**Phenol-coefficient Method.** A method for evaluating water-miscible disinfectants in which a test organism is added to a series of dilutions of the disinfectant; the phenol coefficient is the number obtained by dividing the greatest dilution of the disinfectant killing the test organism by the greatest dilution of phenol showing the same result.

**Phenol Extraction.** Petroleum-refinery solvent-extraction process using phenol as the solvent to remove aromatic, unsaturated and naphthenic constituents from lubricating-oil stocks.

**Phenolphthalein** ( $C_6H_4OH$ )<sub>2</sub>CO $C_6H_5$ CO. Pale-yellow crystals; soluble in alcohol, ether, and alkalis, insoluble in water; used as an acid-base indicator (carminic-colored to alkalis, colorless to acids) for titrations, as a laxative and dye, and in medicine.

**Phenylhydrazine**,  $C_6H_5N_2$ ,  $PhNHNH_2$ . A colourless, refractive oil; b.p. 240–241°C, with slight decomposition. When pure it sets to a crystalline mass at 19°C. It is conveniently purified by crystallization from ether or by distillation in vacuo. It rapidly becomes brown when exposed to air. Sparingly soluble in water, volatile in steam. It forms a stable hydrochloride which can be crystallized unchanged from hot water. It is very poisonous by skin absorption and inhalation of the vapour.

It is prepared commercially by treating benzene diazonium chloride with sodium sulphite and then reducing the mixture



with zinc dust and ethanoic acid. It can also be prepared by reduction of benzene diazonium chloride with  $\text{SnCl}_2$ .

Phenylhydrazine is a strong reducing agent; it reduces Fehling's solution in the cold and reduces aromatic nitro compounds to amines. With ketonic groups, hydrazones are formed. Compounds containing the grouping  $-\text{CHOHCO}-$ , e.g. glucose, fructose, etc., react with two molecules of phenylhydrazine to give osazones.

Phenylhydrazine condenses with acetoacetic ester to give a pyrazolone derivative which on methylation gives phenazone. The sulphonic acid similarly gives rise to the tartrazine dyestuffs. It is used to make indole derivatives by the Fischer process.

**Phenylmagnesium Bromide**  $\text{C}_6\text{H}_5\text{MgBr}$ . A Grignard reagent available as a solution in ether; sp. gr. 1.14.

Derivation : From magnesium and bromobenzene.

Containers : Glass bottles; drums.

Hazard : Dangerous fire risk; solution highly flammable.

Probably toxic.

Use : Arylating agent in organic synthesis.

**Phenylmagnesium Chloride**  $\text{C}_6\text{H}_5\text{MgCl}$ . Available dissolved in tetrahydrofuran.

Hazard : Dangerous fire risk; solution highly flammable.

**pH Measurement.** Determination of the hydrogen-ion concentration in an ionized solution by means of an indicator solution (such as phenolphthalein) or a pH meter.

**Phosphate Buffer.** Laboratory pH reference solution made of  $\text{KH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ ; when 0.025 molal (equimolal of the K and Na salts), the pH is 6.865 at  $25^\circ\text{C}$ .

**Phosphine**  $\text{PH}_3$ . Poisonous, colorless, spontaneously flammable gas with garlic aroma; soluble in alcohol, slightly soluble in cold water; boil at  $-85^\circ\text{C}$ ; used in organic reactions. Also known as hydrogen phosphide; phosphoretted hydrogen.

(DAC-17)

**Phosphor (fluor).** A substance, either organic or inorganic, liquid or crystalline, that is capable of luminescence, that is, of absorbing energy from sources such as x-rays, cathode rays, ultraviolet radiations, alpha particles and emitting a portion of the energy in the ultraviolet, visible or infrared. When the emission of the substance ceases immediately or in the order of  $10^{-8}$  second after excitation, the material is said to be fluorescent. Material that continues to emit light for a period after the removal of the exciting energy is said to be phosphorescent. The half-life of the afterglow varies with the substance and may range from  $10^{-6}$  second to days.

Uses : Fluorescent light tubes; television, radar, and cathode ray tubes; instrument dials; scintillation counters.

**Phosphorescence.** A type of luminescence (q.v.) in which the emission of radiation resulting from excitation of a crystalline or liquid material occurs after excitation has ceased, and may last from a fraction of a second to an hour or more. This phenomenon is characteristic of some organic compounds, as in the firefly, and also of a number of inorganic solid materials, both natural and synthetic. These are used industrially as phosphors.

**Phosphoric Acid  $H_3PO_4$ .** Water-soluble, transparent crystals, melting at  $42^\circ C$ ; used as a fertilizer, in soft drinks and flavor syrups, pharmaceuticals, water treatment, and animal feeds and to pickle and rust-proof metals. Also known as orthophosphoric acid.

**Phosphorus Pentachloride  $PCl_5$ .** Toxic, yellowish crystals, with irritating aroma; an eye irritant; sublimes on heating, but will melt at  $148^\circ C$  under pressure; soluble in carbon disulfide; decomposes in water; used as a catalyst and chlorinating agent. Also known as phosphoric chloride; phosphoric perchloride.

**Phosphorus Thioclhoride  $PSCl_3$ .** Yellow liquid, boiling at  $125^\circ C$ ; used to make insecticides and oil additives.

**Phosphorus Tribromide PBr<sub>3</sub>.** A corrosive, fuming, colorless liquid with penetrating aroma; soluble in acetone, alcohol, carbon disulfide, and hydrogen sulfide; decomposes in water; used as an analytical reagent to test for sugar and oxygen.

**Phosphorus Trichloride PCl<sub>3</sub>.** A colorless, fuming liquid that decomposes rapidly in moist air and water; soluble in ether, benzene, carbon disulfide, and carbon tetrachloride; boils at 76°C; used as a chlorinating agent, phosphorus solvent, and in saccharin manufacture.

**Photoacoustic Spectroscopy.** A spectroscopic technique for investigating solid and semisolid materials, in which the sample is placed in a closed chamber filled with a gas such as air and illuminated with monochromatic radiation of any desired wavelength, with intensity modulated at some suitable acoustic frequency; absorption of radiation results in a periodic heat flow from the sample, which generates sound that is detected by a sensitive microphone attached to the chamber. Abbreviated PAS.

**Photochemical Oxidant.** Any of the chemicals which enter into oxidation reactions in the presence of light or other radiant energy.

**Photochemical Reaction.** A chemical reaction influenced or initiated by light, particularly ultraviolet light, as in the chlorination of benzene to produce benzene hexachloride.

**Photochromic Compound.** A chemical compound that changes in color when exposed to visible or near-visible radiant energy; the effect is reversible; used to produce very-high-density micro-images.

**Photochromic Reaction.** A chemical reaction that produces a color change.

**Photochromism.** The ability of a transparent material to darken reversibly when exposed to light.

Plastics can be made light-sensitive by certain aromatic organic nitro compounds such as 2-(2, 4-dinitrobenzyl) pyridine.

Such chemicals are compatible with most transparent plastics and are either blended with the base resin or applied as coatings.

**Photoconduction.** The phenomenon observed when certain substances, *e.g.* selenium, which are poor conductors of electricity in the dark, become good conductors when exposed to light. Photo-conduction arises from the absorption of light energy causing electrons to be promoted from the valence band of the solid into the conduction band. It is the basis of some commercial photo-copying processes.

**Photocurrent.** An electric current induced at an electrode by radiant energy.

**Photodimerization.** A bimolecular photochemical process involving an electronically excited unsaturated molecule that undergoes addition with an unexcited molecule of the same species.

**Photodisintegration.** The breakup of an atomic nucleus into two or more fragments as a result of bombardment by gamma radiation. Also known as Chadwick-Goldhaber effect.

**Photoelectric Absorption Analysis.** Type of activation analysis in which the  $\gamma$ -photon gives all of its energy to an electron in the crystal under analysis, generating a maximum-sized pulse for that particular  $\gamma$ -energy.

**Photo Electric Colorimeters.** In modern instruments, the intensity of light radiation is measured by using photoelectric cells. The colorimeters with detectors as photoelectric cells are called as photoelectric colorimeters. In these devices the cathode is made of cesium and when light falls on the photocathode, electrons are emitted and the current is measured. The current is a measure of the quantity of light falling on the photocathode. Photoelectric colorimeters contain photo multiplier tubes as detectors for radiations. Photomultiplier tubes are also photo-emissive cells which amplify the electron current several times. The essential parts of a photo electric colorimete are :

(1) A source of radiation such as an incandescent lamp.

- (2) A wavelength control, consisting of filters.
- (3) A sample holder (cuvette) made of transparent glass.
- (4) Photoelectric cells or photo multiplier tubes which act as detectors.
- (5) Recorder, recording absorbance or transmittance of radiations.

**Filters :** Filters are of two types :

- (1) Tinted glass absorption filters made of solid sheet of glass and imparting desired colour to it through a coloured pigment.
- (2) Interference filters : These are produced by depositing a thin metallic film as a sheet of glass. By process of selective reflection, unwanted radiations can be rejected.

There are two models of photo electric colorimeters.

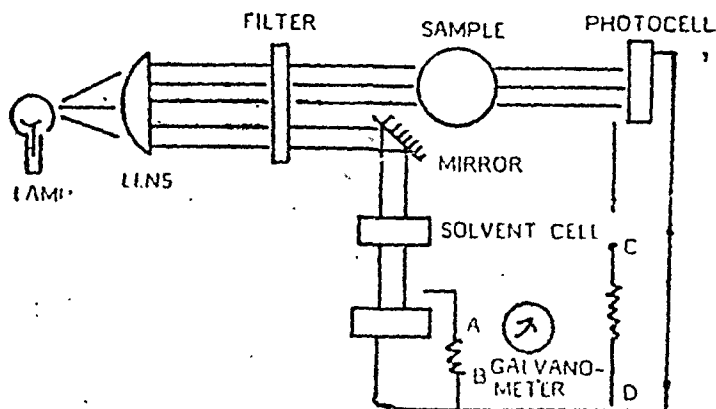
- (1) Single beam type.
- (2) Double beam type.

In single beam type, the blank solution is first adjusted to give 100% transmittance on the scale. The unknown intensity is then determined, after measuring the absorbance. Single beam instruments have a drawback because fluctuations in the voltage supplied to the source changes the intensity of the incident radiation.

In Double beam colorimeters, the fluctuations in the intensity of light due to voltage variations can be compensated by splitting the incident beam into two, one falling on the sample and the other falling on the blank. Light transmitted by the two (Sample and blank) falls on two photocells which produce photocurrents. These currents are passed through two variable resistances AB and CD across which a sensitive galvanometer is connected. A null in the galvanometer indicates that the potentials at AB and CD are same.

To operate such an instrument, a proper filter is first selected. The solvent or blank is first placed in both the cuvettes and the contact A is adjusted to read 100% transmittance. Now if one cuvette is replaced by unknown solution, the radiant

power opposite to the sample cell decreases and hence a potential imbalance occurs which can be measured by moving the contact A to a lower value and hence the transmittance of the solution can be measured.



**Photometry.** Photometric (absorption) methods of analysis depend on the ability of an analyte to selectively absorb light. The analysis of substances based on the measurement of light absorption includes spectroscopy and photocolourimetry.

Spectroscopy is based on the absorbing of monochromatic light, *i.e.* light of a definite wavelength in the visible, ultraviolet, and infrared regions of the spectrum. Different types of spectrometers and spectrophotometers are employed for the light absorption measurements. They always the monochromatic light obtained with the aid of an optical system known as a monochromator.

Absorption in the ultraviolet and visible regions of the spectrum is associated chiefly with the excitation of electrons. The absorption of light in the infrared region of the spectrum is due to molecular vibrations.

Depending on the range of wavelengths used, we distinguish spectroscopy in the ultraviolet region with a wavelength range of 200–400 nm, in the visible region of the spectrum (400–760 nm), and in the infrared region (760–2000 nm). But

the units used for measuring the wavelength of infrared spectra is generally the micrometre ( $1\mu\text{m}=10^{-4}\text{ cm}-10^3\text{ nm}$ ) or the wave number  $\nu$  ( $\text{cm}^{-1}$ ), *i.e.* the number of waves per centimetre.

Spectroscopy in the ultraviolet and visible regions of the spectrum is employed more frequently in pharmaceutical analysis. The method of ultraviolet spectroscopy has been included in the International Pharmacopoeia, and also in the latest editions of the pharmacopoeia of almost all countries for the identification, qualitative and quantitative determination a substance in a drug.

An absorption spectrum is said to be a graphical representation of the amount of light absorbed by a substance at definite wavelengths. To plot a characteristic absorption curve, the values of the wavelengths ( $\lambda$ ) in ultraviolet spectroscopy or of the wave numbers ( $\nu$ ) in infrared spectroscopy are laid off along the axis of abscissas, and the value of the absorbance ( $A$ ), previously known as the optical density, or the per cent transmittance ( $T$ ) (in infrared spectroscopy) along the axis of ordinates.

When plotting the curves of absorption spectra in the ultraviolet and visible parts of the spectrum, the values of the absorptivity (extinction coefficient) or the molar absorptivity can be used. Here  $a$  is the absorption of a solution containing one gram of a substance in 100 mL of its solution at a layer thickness of one centimetre, and  $\Sigma$  is the absorption of a 1 M solution of a substance at a layer thickness of one centimetre. These quantities are determined experimentally and are listed in various tables in the literature for specified wavelengths.

A characteristic of an absorption spectrum is a position of the peaks (minima) of light absorption by the substance, and also the intensity of absorption, which is determined by the optical density  $D$  or absorptivity  $a$  at definite wavelengths.

Ultraviolet spectroscopic measurements are generally conducted in solutions. The solvents mostly used are distilled water, acids, alkalis, alcohols (ethanol, methanol), and some

other organic solvents. The solvent and the analyte must not absorb light in the same region of the spectrum. The form of the latter can change in various solvents, and also when the pH of the medium changes.

The absorption of light by analytes is due to the presence in their molecules of chromophores, which are specific portions of molecules that can absorb radiant energy in the visible or ultraviolet region. They include  $\text{—C=C—}$ ,  $\text{—C}\equiv\text{C—}$ ,  $\text{—COOH}$ ,  $\text{—C=O}$ ,  $\text{=NH}$ ,  $\text{—N=N—}$ ,  $\text{NO}$ ,  $\text{I}$  and  $\text{NO}_2$ , and other functional groups.

Every functional group in a molecule of a substance is characterized by the absorption of light in a definite region of the spectrum, and this property is used for the identification and quantitative determination of a substance in a drug.

In addition to chromophores, a molecule may contain one or more functional groups that themselves do not absorb in the near ultraviolet region being scanned, but can effect the behaviour of the chromophore they are conjugated with. These groups, called auxochromes, usually cause absorption by a chromophore at larger wavelengths and at a higher value of the absorptivity than feature the given chromophore. Examples of auxochromes are  $\text{—SH}$ ,  $\text{—NH}_2$ , and  $\text{—OH}$ .

Infrared spectra for most organic compounds, unlike ultraviolet spectra, are characterized by the presence of a large number of absorption peaks. This is why infrared spectroscopy provides more complete information on the structure and composition of the analyte that enables one to identify compounds very close in structure.

The photocolorimetric method of analysis is based on measuring the absorption of non-monochromatic light by coloured compounds in the visible part of the spectrum.

In case the analytes are colourless, they are converted into coloured compounds by reaction with a suitable reagent. In



this case, the majority of the coloured compounds are complexes or complex ligands. The latter must be stable and have a constant composition and a high colour intensity. Depending on how the concentration of substances in coloured solutions is measured and on the apparatus used, the methods of photocolorimetric analysis are divided into visual and photoelectric ones.

In the visual method, which is also known as colorimetry, the intensity of the colour of the analyte solution is compared with that of standard solution in which the concentration of the substance is known.

The photometric method of analysis (spectroscopy, photocolorimetry) are based on the Bouguer-Lambert-Beer law, which establishes the relation between the absorption of the analyte solution, the concentration of the analyte in this solution, and the thickness of the absorbing layer.

By this law, the absorbance of a solution is directly proportional to the concentration of the absorbent  $C$ , the thickness of the layer  $b$  in centimetres, and the molar absorptivity or absorptivity  $\kappa$  (in the former case,  $\bar{\kappa} = \epsilon$ , and in the latter,  $\kappa = a$ ). This relation is

$$A = \kappa b C$$

or

$$C = \frac{A}{\kappa b}$$

The fundamental principle of operation of photoelectrocolorimeters consists in that light of a definite interval of wavelength passes through a cell with a coloured solution or solvent and falls onto a photoelectric cell that transforms the radiant energy into electrical energy measured by a galvanometer.

**Photoelectrolysis.** The process of using optical energy to assist or effect electrolytic processes that ordinarily require the use of electrical energy.

**Photoelectron Spectroscopy.** The branch of electron spectroscopy concerned with the energy analysis of photoelectrons ejected from a substance as the direct result of bombardment by ultraviolet radiation of x-radiation.

**Photofission.** Fission of an atomic nucleus that results from absorption by the nucleus of a high-energy photon.

**Photographic Photometry.** The use of a comparator-densitometer to analyze a photographed spectrograph spectrum by emulsion density measurements.

**Photohomolysis.** A homolysis reaction in which bond breaking is caused by radiant energy.

**Photolonization.** The removal of one or more electrons from an atom or molecule by absorption of a photon of visible or ultraviolet light. Also known as atomic photoelectric effect.

**Photoisomer.** An isomer produced by photolysis.

**Photoluminescence.** Luminescence stimulated by visible, infrared, or ultraviolet radiation.

**Photolysis.** The use of radiant energy to produce chemical changes.

**Photomechanochemistry.** A branch of polymer sciences that deals with photochemical conversion of chemical energy into mechanical energy.

**Photometric Analysis.** Chemical analysis by means of absorption or emission of radiation, primarily in the near ultraviolet, visible, and infrared portions of the electromagnetic spectrum. It includes such techniques as spectrophotometry, spectrochemical analysis, Raman spectroscopy, colorimetry and fluorescence measurements.

**Photon.** The unit (quantum) of electromagnetic radiation. Light waves, gamma rays, x-rays, etc., consist of photons. Photons are discrete concentration of energy that have no rest mass and move at the speed of light. Their nature can be described only in mathematical terms. Photons are emitted when electrons move from one energy state to another, as in an excited atom.

**pH(S).** See pH standard.

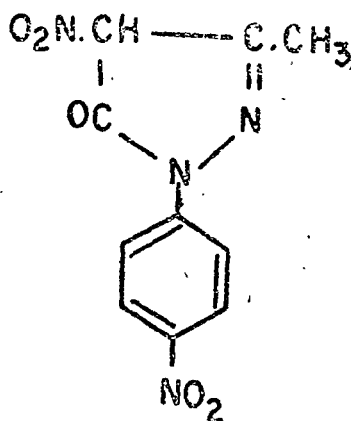
**pH Standard.** Five standard laboratory solutions available from the U. S. National Bureau of Standards, each solution having a known pH value; the standards cover pH ranges from 3.557 to 8.833. Abbreviated pH (S).

**Phthalate Buffer.** Laboratory pH reference solution made of potassium hydrogen phthalate,  $\text{KHC}_8\text{H}_4\text{O}_4$ ; at 0.05 molal, the pH is 4.008 at  $25^\circ\text{C}$

**Physical Property.** Property of a compound that can change without involving a change in chemical composition; examples are the melting point and boiling point.

**Pico.** Prefix meaning  $10^{-12}$  unit (symbol=p). 1. pg = 1 picogram =  $10^{-12}$  gram.

**Picrolonic Acid Reagent.** Calcium salts form characteristic crystalline ppt. with the reagent.



Test Place 1 drop of a cold saturated (1% aqueous) solution of reagent on a warm microscope slide, add 1 drop of the test solution.

Characteristic rectangular crystals indicate calcium, the limit of identification being  $0.01 \mu\text{g Ca}$ ; conc. limit, 1 in 50,000.

**Piezoechemistry.** The field of chemical reactions under high pressures.

**Pilot Plant.** A trial assembly of small-scale reaction and processing equipment which is the intermediate stage between laboratory experiment and full-scale operation in the development of a new product. The functions of this stage are :

1. To furnish chemical engineers with design data needed to construct a large-scale plant;
2. To resolve the many problems inherent in conversion from batch to continuous production;
3. To eliminate the differences that accompany change from constant laboratory conditions to a less closely controlled environment; and
4. To provide management with a basis for cost evaluation and estimation of the capital requirements of the new product. As the size of the pilot plant varies with the nature of the product, it must be determined on an individual basis.

**Pilot-scale Chemical Reaction.** Small-scale chemical reaction used to test operating conditions and product yields; used as a pilot for design of large-scale reaction systems.

**Pipette (pipet).** A slender glass tube open at both ends and having an expanded area at or near the center designed to contain a specific volume of liquid, e.g., 5 cc. Liquid is drawn into the tube by oral suction. Used in transferring measured volumes of liquid from one container to another.

**Pipet.** Graduated or calibrated tube which may have a center reservoir (bulb); used to transfer known volumes of liquids from one vessel to another; types are volumetric or transfer, graduated, and micro.

**Pitzer Equation.** Equation for the approximation of data for heats of vaporization for organic and simple inorganic compounds; derived from temperature and reduced temperature relationships.

**PK.** A measurement of the completeness of an incomplete chemical reaction. It is defined as the negative logarithm (to the base 10)

of the equilibrium constant,  $K$ , for the reaction in question. The  $pK$  is most frequently used to express the extent of dissociation or the strength of weak acids, particularly fatty acids, weak acids, and also complex ions, or similar substances. The weaker an electrolyte the larger its  $pK$ .

**Planck's Constant,  $h$ .** The constant relating the energy and frequency of radiation,  $E=h\nu$ . It has a value of  $6.6256 \times 10^{-27}$  erg.sec.

**Plasma Desorption Mass Spectrometry.** A technique for analysis of nonvolatile molecules, particularly heavy molecules with atomic weight over 2000, in which heavy ions with energies on the order of 100 MeV penetrate and deposit energy in thin films, giving rise to chemical reactions that result in the formation of molecular ions and shock waves that result in the ejection of these ions from the surface; the ions are then analyzed in a mass spectrometer. Abbreviated PDMS.

**Plasma-jet Excitation.** The use of a high-temperature plasma jet to excite an element to provide measurable spectra with many ion lines similar to those from spark-excited spectra.

**Plate Efficiency.** The equilibrium produced by an actual plate of a distillation column or countercurrent tower extractor compared with that of a perfect plate, expressed as a ratio.

**Plate Theory.** In gas chromatography, the theory that the column operates similarly to a distillation column; for example, chromatographic columns are considered as consisting of a number of theoretical plates, each performing a partial separation of components.

**Plate Tower.** A distillation tower along the internal height of which is a series of transverse plates (bubble-cap or sieve) to force intimate contact between downward flowing liquid and upward flowing vapour.

**Plate, Tray.** The vapour-liquid contacting units in an absorption or fractionating column.

**Plate Column, Tray Column.** The plate column, or tray column as it is known in the U.S., is the plant most widely used for vapour-liquid contacting, and as such is employed in gas absorption and stripping and for fractional distillation. It consists of a vertical cylindrical column containing a series of horizontal plates or trays spaced up to 1 m apart and set one above the other all the way up the column. Liquid flows down the column from plate to plate and vapour passes upwards through holes in them. Vapour-liquid contacting is by bubbles of vapour passing upwards through the pools of liquid on the plates, these pools being maintained by means of weirs at the liquid inlet and outlet on the plates. Liquid is carried from one plate to the next usually, but not invariably, by ducts called downcomers. There are a number of types of plate in use, but the operation of most of them is similar.

Since the transfer of material between phases takes place on the plates, the degree of gas absorption, or of separation in the case of a distillation column, depends directly on their number. The latter is therefore dependent on the required duty.

Plate columns are always used for large-scale operation; diameters range up to 7 m or so and heights in excess of 35 m are not uncommon.

**pNa.** Logarithm of the sodium-ion concentration in a solution; that is  $pNa = -\log a_{Na^+}$ , where  $a_{Na^+}$  is the sodium-ion concentration.

**POD Analysis.** A precision laboratory distillation procedure used to separate low-boiling hydrocarbon fractions quantitatively for analytical purposes. Also known as Podbielniak analysis.

**Podbielniak Extractor.** A solvent-extraction device in which centrifugal action enhances liquid-liquid contact and increases resultant separation efficiency.

**Polarimetry.** The polarimetric method of analysis depends on the ability of substances to rotate the plane of polarization when polarized light passes through them. Substances rotating the plane of polarization of light are called optically active.

If the plane of polarization rotates to the right (clockwise), the substance is said to be dextrorotatory (from the Latin *dexter*—right), and its name is preceded by the prefix sign (+) or the letter *d*; if the plane of polarization rotates to the left (anticlockwise), the substance is said to be levorotatory (from the Latin *laevus*—left), and its name is preceded by the prefix sign(−) or the letter *l*.

The deflection of the plane of polarization from the initial position expressed in angular degrees is known as the angle of rotation and is designated by the Greek letter  $\alpha$ . The angle of rotation depends on the nature of the optically active substance, its layer thickness, temperature, the nature of the solvent, and the wavelength of the light. The optical rotation is generally determined at 20°C and at the wavelength of the sodium spectrum D line (589.3 nm).

The optical activity of a substance is characterized by the specific rotation, *i.e.* the rotation of the plane of polarization produced by a layer of the substance 1 dm thick at a concentration of 1g/mL at 20°C. The specific rotation of solutions is evaluated by the formula

$$[\alpha]_D^{20} = \frac{\alpha \times 100}{lC}$$

where  $\alpha$  is the measured angle of rotation, deg,  $l$  is the thickness of the solution layer, dm, and  $C$  is the concentration of the solution, percent.

Knowing the specific rotation of a substance, which is constant within a define interval of concentrations, one can find out its content ( $C$ ) in the solution in per cent by the formula

$$C = \frac{\alpha \times 100}{[\alpha]_D^{20} l}$$

For liquid substances, the specific rotation is

$$[\alpha]_D^{20} = \frac{\alpha}{l \rho}$$

where  $\rho$  is the density of the liquid, g/cm<sup>3</sup>.

Polarimetry is widely employed in pharmaceutical analysis to establish the optical activity of drugs, their quality and content.

Instruments known as polarimeters are used to measure the angle of rotation of the plane of polarization. A variety of polarimeters are available, but their principle of operation is the same.

**Polarization Spectroscopy.** A type of saturation spectroscopy in which a circularly polarized saturating laser beam depletes molecule with a certain orientation preferentially, leaving the remaining ones polarized; the latter are detected through their induction of elliptical polarization in a probe beam, allowing the beam to pass through crossed linear polarizers.

**Polarized Scattering.** In a quasielastic light scattering experiment performed with polarizers, the type of scattering produced when the polarizers select both the incident and final polarizations perpendicular to the scattering plane.

**Polarogram.** Plotted output (current versus electrode voltage) for polarographic analysis of an electrolyte.

**Polarographic Analysis.** An electroanalytical technique in which the current through an electrolysis cell is measured as a function of the applied potential; the apparatus consists of a potentiometer for adjusting the potential, a galvanometer for measuring current, and a cell which contains two electrodes, a reference electrode whose potential is constant and an indicator electrode which is commonly the dropping mercury electrode. Also known as polarography.

**Polarographic Cell.** Device for polarographic (voltammetric) analysis of an electrolyte solution; a known voltage is applied to the solution, and the ensuing current that passes through the cell (to an electrode) is measured.

**Polarographic Maximum.** A deceptively high voltage buildup on an electrode during polarographic analysis of an electrolyte; caused by a reduction or oxidation process at the electrode.



**Polarography.** Polarography is a particular case of the general electroanalytical technique known as voltametry which involves the study of current voltage relationships in electrolysis. The electrolysis is carried out by using one electrode of large surface area (non-polarisable electrode) and another electrode having a small surface area (polarisable electrode) or the microelectrode. When this micro-electrode is dropping mercury electrode (D.N.E.) the technique is called polarography.

#### Working of Dropping Mercury Electrode :

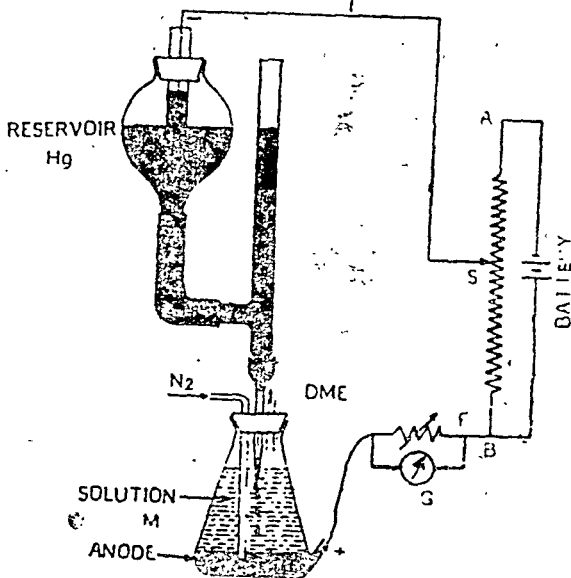


Fig. 28

The cathode and anode are connected to the negative and positive terminals respectively of a battery. The applied voltage is varied by sliding contact 5 on potentiometric wire AB. The galvanometer G shows the current strength. A shunt F allows the sensitivity of the instrument to be varied as required. The experimental solution is taken in the container M. The anode pool is in this vessel. N<sub>2</sub> is passed through the solution to remove dissolved oxygen.

When mercury drop falls into the solution and the potential of the DME is adjusted to the reduction potential of the metal ion, these metal ions get reduced and form an amalgam with mercury. The metal ions in solution move towards cathode due to electrostatic attraction. The reduction of the ion at the cathode causes a decrease in concentration of the ions in the vicinity of the cathode. A concentration gradient is established between the droplet near the cathode and the concentration in the bulk of the solution.

The advantages and disadvantages of dropping mercury electrode are as follows :

- (i) DME eliminates passivity and effects due to poisoning as its surface is smooth, reproducible and continuously renewable.
- (ii) The high voltage helps in reduction of metal ions.
- (iii) Metals form amalgam with mercury.
- (iv) It can be used with saturated calomel electrode over the range of 0.4 to  $-2$  volts.
- (v) The diffusion current attains a steady value after each change of applied voltage.
- (vi) The concentration change in the bulk of the solution is negligible.
- (vii) A series of reducible species can be estimated in one solution as the electrode is continuously renewed.

Disadvantages of dropping mercury electrode :

- (i) This electrode generates some small currents like residual current, migration current, diffusion current, kinetic current which adds to the error in current measurement.
- (ii) The liquid used is mercury which is costly and poisonous.
- (iii) Since the drop is growing its area is constantly changing, hence the current passing through the cell increases as the drop grows and drops to zero as the drop breaks.

**Polymeric Reagents.** Solid, insoluble reagents for organic synthesis produced by introducing typical organic functional groups *e.g.*, Br, Li,  $\text{SO}_3\text{H}$ ,  $\text{CH}_2\text{Cl}$ ] on to a small proportion of benzene rings

of cross-linked polystyrene. They allow selective, reactivity, simplified reaction work-up (filtration) and high purity product isolation, low volatility of noxious reagents and polymer recycling. Catalyst systems in which active groups, e.g.  $\text{PR}_3$ , co-ordinated to metals and substituted on to a polymer are also available.

**Polysulfide Treating.** A petroleum-refinery process used to remove elemental sulfur from refinery liquids by contacting them with a nonregenerable solution of sodium polysulfide.

**Population Inversion.** The condition in which a higher energy state in an atomic system is more heavily populated with electrons than a lower energy state of the same system.

**Postignition.** Surface ignition after the passage of the normal spark.

[ **Post precipitation.** Precipitation of an impurity after the process of primary precipitate is called as Post-precipitation. For example when acid solution of Ammonium oxalate is added of acidic solution of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  ions, first calcium oxalate precipitate followed by Mg Oxalate if the concentration of  $\text{Mg}^{+2}$  is high.

Removal of contamination of precipitates :

- (1) Removal of interfering ions prior to precipitation so that contamination by coprecipitation involving occlusion is minimized. These ions can be converted into a non-interfering form.
- (2) Addition of dilute solution of precipitating agent, to the hot solution of reacting ions.
- (3) Addition of flocculating electrolyte such that it does not seriously contaminate the precipitate by adsorption.
- (4) Digestion time is restricted in Post-precipitation conditions.
- (5) Contamination by coprecipitation through adsorption is removed by reprecipitation method.
- (6) Proper concentration of electrolyte in the wash to remove peptization in the case of gelatinous precipitates.

**Potassium Chlorate**  $\text{KClO}_3$ . Transparent, colorless crystals or a white powder with a melting point of  $356^\circ\text{C}$ ; soluble in water, alcohol, and alkalis; used as an oxidizing agent.

**Potassium Chromate**  $\text{K}_2\text{CrO}_4$ . Yellow crystals, melting at  $971^\circ\text{C}$ ; soluble in water, insoluble in alcohol; used as an analytical reagent and textile mordant, in enamels, inks, and medicines, and as a chemical intermediate.

**Potassium Chromate Reagent**. Silver salts form red ring with the reagent.

Test Place a drop of the test solution on spot plate, add one drop of  $(\text{NH}_4)_2\text{CO}_3$  solution and stir. Remove one drop of the clear liquid and place it on filter paper and add one drop of the reagent solution (1% solution in  $\text{N CH}_3\text{COOH}$ ).

A red ring indicates Ag, the limit of identification being  $2 \mu\text{g Ag}$ ; conc. limit, 1 in 25,000.

**Potassium Dichromate** (potassium bichromate; red potassium chromate)  $\text{K}_2\text{Cr}_2\text{O}_7$ .

Properties: Bright, yellowish red transparent crystals; bitter, metallic taste. Soluble in water; insoluble in alcohol. Sp. gr. 2.676 ( $25^\circ\text{C}$ ); m.p.  $396^\circ\text{C}$ ; b.p., decomposes at  $500^\circ\text{C}$ .

Derivation: Reaction of potassium chloride and sodium dichromate.

Grades: Commercial; highest purity; highest purity fused; reagent.

Containers: 100-lb bags; 400-lb drums.

Hazard: Toxic by ingestion and inhalation. Dangerous fire risk in contact with organic materials. Strong oxidizing agent.

Uses: Oxidizing agent (chemicals, dyes, intermediates); analytical reagent; brass pickling compositions; electroplating; pyrotechnics; explosives; safety matches; textiles; dyeing and printing; chrome glues and adhesives; chrome tanning leather;

wood stains; poison fly paper; process engraving and lithography; synthetic perfumes; chrome alum manufacture; pigments; alloys; ceramic products; depolarizer in dry cell batteries; bleaching fats and waxes.

**Potassium Ferrocyanide** (yellow prussiate of potash; yellow potassium prussiate)  $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ .

Properties : Lemon yellow crystals or powder; mild saline taste; effloresces on exposure to air. Soluble in water; insoluble in alcohol. Sp. gr. 1.853 (17°C); m.p. loses its water of crystallization when heated to 70°C; b.p., decomposes.

Derivation : From nitrogenous waste products, iron filings and potassium carbonate.

**Potassium Iodate**  $\text{KIO}_3$ . Odorless, white crystals; soluble in water; insoluble in alcohol; melts at 560°C; used as an analytical reagent and in medicine.

**Potassium Iodide**  $\text{KI}$ . Water- and alcohol-soluble, white crystals with saline taste; melts at 686°C; used in medicine and photography, and as an analytical reagent.

**Potassium Manganate**  $\text{K}_2\text{MnO}_4$ . Water-soluble dark-green crystals, decomposing at 190°C; used as an analytical reagent, bleach, oxidizing agent, disinfectant, mordant for dyeing wool and in photography, printing, and water purification.

**Potassium Molybdate**  $\text{K}_2\text{MoO}_4$ .

Properties : White, microcrystalline powder; deliquescent; soluble in water; insoluble in alcohol; sp. gr. 2.91 (18°C); m.p. 919°C.

Use : Reagent.

**Potassium Osmate** (potassium perosmate)  $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ .

Properties : Violet crystals. Hygroscopic. Soluble in water; insoluble in alcohol and ether.

Hazard : Toxic by ingestion and inhalation.

Use : Determination of nitrogenous matter in water.

**Potassium Perchlorate**  $\text{KClO}_4$ . Explosive, oxidative, colorless crystals; soluble in water, insoluble in alcohol; decomposes at  $400^\circ\text{C}$ ; used in explosives, medicine, pyrotechnics, analysis, and as a reagent and oxidizing agent. Also known as potassium hyperchlorate.

**Potassium Permanganate**  $\text{KMnO}_4$ . Highly oxidative, water-soluble, purple crystals with sweet taste; decomposes at  $240^\circ\text{C}$ ; and explodes in contact with oxidizable materials; used as a disinfectant and analytical reagent, in dyes, bleaches, and medicines, and as a chemical intermediate. Also known as purple salt.

**Potassium Thiocyanate**  $\text{KCNS}$ . Water and alcohol soluble, colorless, odorless hygroscopic crystals with saline taste; decomposes at  $500^\circ\text{C}$ ; used as an analytical reagent and in freezing mixtures, chemicals manufacture, textile printing and dyeing, and photographic chemicals. Also known as potassium rhodanide; potassium sulfocyanate; potassium sulfocyanide.

**Potentiometric Cell.** Container for the two electrodes and the electrolytic solution being titrated potentiometrically.

**Potentiometric Titrations.** In potentiometric titration, the principle involved is the dependence of electrode potential on the activity or the concentrations of the ions with which the electrode is reversible. An equation is given by Nernst. This equation at  $25^\circ\text{C}$  and in terms of logarithm to base 10 is,

$$E = E^\circ - \frac{0.0592}{n} \log \frac{a(\text{oxidised state})}{a(\text{reduced state})}$$

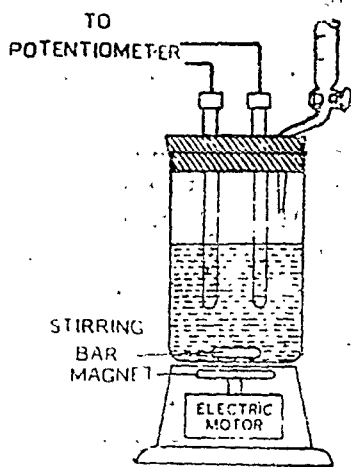
Where  $a(\text{oxidised})$  and  $a(\text{reduced})$  represent the products of the activities of all the species involved in the oxidised and reduced states respectively.  $n=1$  for univalent ions,  $n=2$  for bivalent ions, etc. For titrating an acid against a base a cell is set up by combining a hydrogen electrode with a reference electrode such as calomel electrode through a salt bridge. Calomel electrode is called as reference electrode.

$\text{Pt}/\text{H}_2$  (1 atm.)/ $\text{H}^+$  (Solution)//saturated calomel-electrode. Here hydrogen electrode is an indicator electrode. The emf of

the cell is the algebraic sum of the two electrode potentials. In the start of the titration, the potential change is small. At end point there is a rapid change in potential. Thus the end point is determined by finding the quantity of titrant added at the point at which the rate of change of potential is maximum.

Give a schematic description of the apparatus and procedure for carrying out a potentiometric titration ore as follows :

The apparatus required for potentiometric titrations is in the adjacent figure. One of the electrodes is of constant reference electrode and the other is an indicator electrode. It is necessary to stir the solution after each addition of the titrant. This is usually done by a mechanical or magnetic stirrer. First the emf of the cell is determined. Emf is also determined after each addition of the titrant (normally 1 ml at a time). It is also necessary to give sufficient time to reach equilibrium after every addition of the titrant. This is done to get a constant potential of the cell. The end point of the titration is then determined graphically by plotting Emf vs Volume of titrant

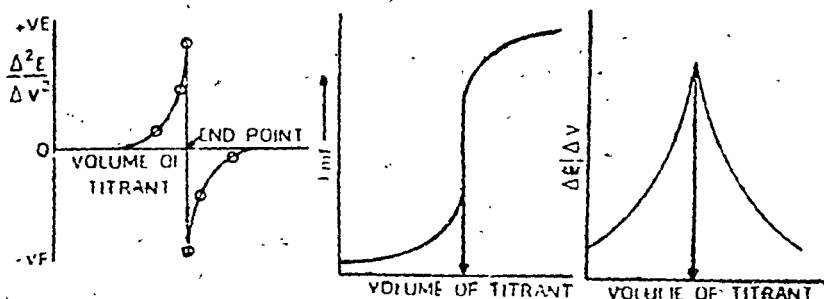


added, or  $\Delta E / \Delta V$  vs. volume of titrant added.  $\Delta E^2 / \Delta V^2$  vs. volume of titrant added.

The different ways of determining end point in potentiometric titrations are as follows :

First the emf values corresponding to different volumes of titrant added are recorded. A graph of emf against volume of titrant added is plotted as shown below. If the curve is vertical near the end point region then the end point can be determined easily by bisecting the nearly straight line portion of the curve.

If in the above, the line obtained is not vertical then a graph of  $\Delta E/\Delta V$  against volume of titrant is plotted. The peak position in this graph gives the value of the end point. The end point can also be located by plotting the second derivative  $\Delta^2 E/\Delta V^2$  against volume of titrant. This method is based on the fact that the second derivative is zero at the point at which the first derivative  $\Delta E/\Delta V$  is maximum.



**Powder Diffraction Camera.** A metal cylinder having a window through which an x-ray beam of known wavelength is sent by an x-ray tube to strike a finely ground powder sample mounted in the center of the cylinder; crystal planes in this powder sample diffract the x-ray beam at different angles to expose a photographic film that lines the inside of the cylinder; used to study crystal structure. Also known as x-ray powder diffractometer.

**Powder Pattern.** In the powder method of x-ray diffraction analysis, the display of lines made on film by the Debye-Scherrer method or on paper by a recording diffractometer.



**ppm.** Abbreviation for parts per million, used to indicate extremely minute concentrations of particulates in liquids and gases.

**Prandtl Number.** For any substance, the ratio of the viscosity to the thermal conductivity. The lower the number, the higher is the convection capacity of the substance. This ratio is important in heat and chemical engineering calculations.

**Precession Camera.** An x-ray diffraction camera used in the Buerger precession method for recording the diffractions of an individual crystal.

**Precipitant.** A chemical or chemicals that cause a precipitate to form when added to a solution.

**Precipitate.** Small particles that have settled out of a liquid or gaseous suspension by gravity, or that result from a chemical reaction; precipitated compounds such as blanc fixe (barium sulfate) are prepared in this way, for example, by the reaction  $\text{BaCl} + \text{NaSO}_4 \rightarrow \text{NaCl} + \text{BaSO}_4$ . In formulas a downward vertical arrow ( $\downarrow$ ) is sometimes used to indicate a precipitate. A class of organic pigments called lakes are made by precipitating an organic dye onto an inorganic substrate. Colloidal particles dispersed in a gas, as flue dust in industrial stacks, can be precipitated by introducing an electric charge opposite to that which sustains the particles.

**Precipitate Electrode.** See ion-selective electrodes.

**Precipitation.** The formation of an insoluble compound from solution either by interaction of two salts, e.g.



or by temperature change effecting solubility. The formation of a precipitate is governed by the solubility product. In analysis precipitation is important in gravimetric and some forms of qualitative analysis. The form and purity of the precipitate depends upon the conditions used for the precipitation. Easily filtered precipitates are frequently formed by use of compounds which slowly release the precipitating reagent.

**Precipitation Hardening, Age Hardening.** The hardening of certain alloys which takes place with time when a supersaturated solution tends to decompose with partial precipitation of the solute metal as an intermetallic compound. The first stages remove dislocations to give an increase in hardness and decrease in ductility. Duralumin (Al+4% Cu) exhibits age hardening after quenching from 480°C.

**Precipitation Indicator.** An indicator which functions by giving a coloured precipitate at the end-point. Thus  $K_2CrO_4$  is used as indicator in the estimation of  $Cl^-$  by  $Ag^+$ ; at the end-point there is a red precipitate of  $Ag_2CrO_4$ .

**Precipitation.** The process of producing a separable solid phase within a liquid medium; represents the formation of a new condensed phase, such as a vapor or gas condensing to liquid droplets; a new solid phase gradually precipitates within a solid alloy as a result of slow, inner chemical reaction; in analytical chemistry, precipitation is used to separate a solid phase in an aqueous solution.

**Precipitation Number.** The number of milliliters of asphaltic precipitate formed when 10 milliliters of petroleum-lubricating oil is mixed with 90 milliliters of a special-quality petroleum naphtha, then centrifuged according to ASTM test conditions; used to determine the quantity of asphalt in petroleum-lubricating oil.

**Precipitation From Homogeneous Solution.** In this technique, the precipitating reagent is slowly generated in the solution through an auxiliary reaction. The slow addition of reagent to the hot solution of a sample will tend to produce conditions of low supersaturation. The solvent remains homogenous with respect to both the ion being precipitated and the reagent at all times during the process of precipitation. By changing the rate of chemical reaction, producing the precipitant in homogeneous solution, the required particle size of the precipitate can be obtained. Coprecipitation is also minimised in this process.

For example, urea hydrolyses slowly on boiling, producing  $\text{NH}_3$  and carbondioxide.



Urea hydrolysis method can be used in the precipitation of  $\text{Ba}^{+2}$  as  $\text{BaCrO}_4$  in the presence of Ammonium Acetate. Precipitation of  $\text{Al}^{+3}$  as the oxilate.

Precipitation of  $\text{Ni}^{+2}$  as dimethyl glyoximate.

Urea hydrolysis method can also be used to precipitate  $\text{Ca}(\text{II})$  and Oxalate ion. Similarly  $\text{SO}_4^{-2}$  ion can be generated by the hydrolysis of sulphonic acid.

Similarly sulphide ions can be released from acidified solution of sodium thio-sulphate and phosphate ions can be released from the hydrolysis of trimethyl phosphate.

**Precipitation Titration.** Amperometric titration in which the potential of a suitable indicator electrode is measured during the titration.

**Precision and Accuracy.** Precision is a measure of reproducibility of results. Accuracy is a measure of the degree of exactness of a measurement to an accepted standard. Precision denotes the extent of agreement amongst themselves, between the numerical values of a set of measurements, of a property made in an identical manner. Accuracy denotes the closeness of a measurement of a property to the accepted value of the property. Accuracy is expressed by absolute error or relative error. Precision is expressed by the deviation of the value from the mean or median of a set of values. The difference between the highest and lowest value is called the spread or range and this is also another method of expressing precision of the value. Precision is also expressed by the relative average deviation from the mean or

$$\text{Relative Average Deviation} = \frac{\text{Average Deviation from Mean or Median}}{\text{Mean or Median}}$$

**Predissociation.** The dissociation of a molecule that has absorbed energy before it can lose energy by radiation.

**Proximate Analysis.** A technique that separates and identifies categories of compounds in a mixture; reported are moisture and ash content, the extracts of the mixture made with alcohol, petroleum ether, water hydrochloric acid and resins, starches, reducing sugars, proteins, fats, esters free, acids, so on; this type of analysis of solid fuels allows a prediction to be made as to how the fuel will behave in a furnace.

**Proximate Analysis of Coal.** The determination of specific properties of coal relating to its use as a fuel. Moisture content, volatile matter, ash, carbon, calorific value sulphur content agglutinating value are usually determined in specific but arbitrary tests.

**Puking.** In a distillation column, the foaming and rising of liquid so that part of it is driven out of the vessel through the vapor line.

**Pulse Column.** Continuous-phase process column (such as liquid only or gas only) in which the flow-through is pulsating used to increase mass-transfer rates, as in a liquid-liquid extraction operation.

**Pulsed-bed Sorption.** Solid-liquid countercurrent adsorption process (such as an ion-exchange process) in which the granulated solids bed and the solution flow alternately, in opposite directions.

**Pulser.** Device used to create a pulsating fluid, flow through a process vessel, such as a liquid-liquid or vapor-liquid extraction tower; used to increase contact and mass transfer rates.

**Pulse Radiolysis.** A method of studying fast chemical reactions in which a sample is subjected to a pulse of ionizing radiation, and the products formed by the resulting reactions are studied spectroscopically.

**Pumparound.** A system or process vessel that moves liquid out of and back into the vessel at a new location; for example, in a bubble tower, the withdrawing of liquid from a plate or tray, followed by cooling, and returning to another plate to induce condensation of vapors.

**Purity.** The state of a chemical compound when no impurity can be detected by any experimental method; absolute purity is never reached in practice.

**Purity, Chemical.** A substance is said to be pure when its physical and chemical properties coincide with those previously established and recorded in the literature, and when no change in these properties occurs after application of the most selective fractionation techniques. In other words, purity exists when no impurity can be detected by any experimental procedure. There are a number of recognized standards of purity.

**Putrefaction.** Decomposition of organic matter, particularly the anaerobic breakdown of proteins by bacteria, with the production of foul-smelling compounds.

**Pyknometer.** An instrument for measuring the density of a substance by determining the weight of a known volume. A specific gravity bottle is the simplest form of pyknometer.

**Pyrex.** A trade name for a heat-resisting borosilicate glass containing a high percentage of  $\text{SiO}_2$  with some B, Al and alkalis. Pyrex has high mechanical strength, resists attacks by strong acids and alkalis, and withstands sudden changes of temperature without breakage; it softens at a higher temperature than ordinary soda glasses.

## Q

**Quad.** An energy unit that has come into use in recent year in predicting future energy requirements on a national basis. One quad equals  $10^{15}$  Btu, which is the energy equivalent of  $10^{12}$  cubic feet of natural gas, or 182 million barrels of oil, or 42 million tons of coal, or 293 billion kw-hr of electricity.

**Quadratic Stark Effect.** A splitting of spectral lines of atoms in an electric field in which the energy levels shift by an amount proportional to the square of the electric field, and all levels shift to lower energies; observed in lines resulting from the lower energy states of many-electron atoms.

**Quadratic Zeeman Effect.** A splitting of spectral lines of atoms in a magnetic field in which the energy levels shift by an amount proportional to the square of the magnetic field.

**Quadruple Point.** Temperature at which four phases are in equilibrium, such as a saturated solution containing an excess of solute.

**Quadrupole Spectrometer.** A type of mass spectroscopy in which ions pass along a line of symmetry between four parallel cylindrical rods; an alternating potential superimposed on a steady potential between pairs of rods filters out all ions except those of a predetermined mass. Also known as *Massenfilter*.

**Qualitative Analysis.** Qualitative analysis is mainly concerned with the electron and identification of constituents of an inorganic substance or a mixture of substances. The inorganic mixture given for analysis is made from such components which, on dissolving in water, split up into two types of charged particles, one type carrying a negative charge called the anion or negative ion and the other carrying a positive charge known as cation or positive ion. The cation is also called a basic radical whereas the anion is called the acidic radical. In potassium chloride, potassium ion is a basic radical whereas the chloride ion is an acidic radical.

**Quantitative Analysis.** The analysis of a gas, liquid, or solid sample or mixture to determine the precise percentage composition of the sample in terms of elements, radicals, or compounds.

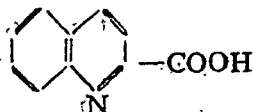
**Quartet.** A group of four closely spaced lines in a spectrum (in n.r., etc.).

**Quenching.** Phenomenon in which a very strong electric field, such as a crystal field, causes the orbit of an electron in an atom to pro-

cess rapidly so that the average magnetic moment associated with its orbital angular momentum is reduced to zero.

**Quevenne Scale.** Arbitrary scale used with hydrometers or lactometers in the determination of the specific gravity of milk; degrees Quevenne = 1000 (specific gravity - 1).

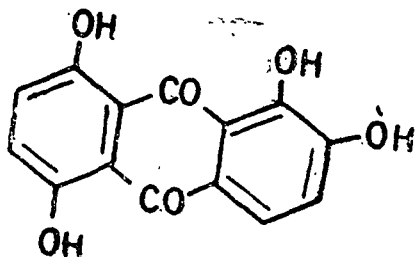
**Quin Aldic Acid Reagent.** Zinc salts form white ppt. with the reagent.



The interference is due to Cu, Cd, Fe and Cr.

**Test.** Take 2 drops of the test solution in a semi-micro test tube and add 2 drops of the reagent solution (1 g. of the reagent is neutralized with NaOH and then diluted to 100 mL with distilled water).

**Quinalizarin Reagent.** Aluminium salts give red-violet colour with the



reagent.

**Test.** Place 1 drop of the test solution on a prepared filter paper. (A suitable filter paper is prepared by soaking filter paper in a solution of 10 mg of the reagent in 2 mL of pyridine and 20 mL acetone). Hold the paper over ammonia when it will turn blue due to formation of the ammonium salt of the dye. Now hold the paper over glacial acetic acid until the unmoistened paper regains its brown colour.

A red-violet spot on the paper indicates aluminium, the limit of identification being 0.01  $\mu\text{gAl}$ ; conc. limit, 1 in 2,000,000.

# R

**Racemic Mixture.** A compound which is a mixture of equal quantities of dextrorotatory and levorotatory isomers of the same compound, and therefore is optically inactive.

**Radial Chromatography.** A circular disk of absorbent paper which has a strip (wick) cut from edge to center to dip into a solvent; the solvent climbs the wick, touches the sample, and resolves it into concentric rings (the chromatogram). Also known as circular chromatography; radial-paper chromatography.

**Radial-paper Chromatography.** See radial chromatography.

**Radical**

- (1) An ionic group having one or more charges, either positive or negative, e.g.,  $\text{OH}^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ .
- (2) See free radical.

**Radiofunctional Name.** A name for an organic compound that uses two key words; the first word corresponds to the group or groups involved and the second word indicates the functional group—for example, alkyl halide.

**Radioassay.** An assay procedure involving the measurement of the radiation intensity of a radioactive sample.

**Radiochemical Laboratory.** A specifically equipped and shielded chemical laboratory designed for conducting radiochemical studies without danger to the laboratory personnel.

**Radio-frequency Spectrometer.** An instrument which measures the intensity of radiation emitted or absorbed by atoms or molecules as a function of frequency at frequencies from  $10^5$  to  $10^9$  hertz; examples include the atomic-beam apparatus, and instruments for detecting magnetic resonance.

**Radio-frequency Spectroscopy.** The branch of spectroscopy concerned with the measurement of the intervals between atomic



or molecular energy levels that are separated by frequencies from about  $10^5$  to  $10^9$  hertz as compared to the frequencies that separate optical energy levels of about  $6 \times 10^{14}$  hertz.

**Radiometric Analysis.** Quantitative chemical analysis that is based on measurement of the absolute disintegration rate of a radioactive component having a known specific activity.

**Radiametric Titration.** Use of radioactive indicator to track the transfer of material between two liquid phases in equilibrium, such as titration of  $^{110}\text{AgNO}_3$  (silver nitrate, with the silver atom having mass number 110) against potassium chloride.

**Raman, Chandrasekhara (1888-1970).** Indian academic spectroscopist. Researches by Raman into optical diffraction and Scattering led to his observation of the effect that is now known by his name. Raman's widespread researches also included study of the lattice vibrations of crystals and the optical properties of gemstones.

**Raman Spectropotometry.** The study of spectral-line patterns on a photograph taken at right angles through a substance illuminated with a quartz mercury lamp.

**Raman Spectroscopy.** Analysis of the intensity of Raman scattering of monochromatic light as a function of frequency of the scattered light.

**Raman Spectrum.** A display, record, or graph of the intensity of Raman scattering of monochromatic light as a function of frequency of the scattered light.

**Ramsauer Effect.** The vanishing of the scattering cross section of electrons from atoms of a noble gas at some value of the electron energy, always below 25 electronvolts.

**Ramsbottom Coke Test.** A laboratory test for carbon residue in petroleum products.

**Raney Nickel.** A special form of nickel prepared by treating an Al-Ni alloy with NaOH solution. The nickel is left in a spongy mass which is pyrophoric when dry. This form of nickel is a most powerful catalyst, especially for hydrogenations.

**Raoult's Law.** The law that the vapor pressure of a solution equals

the product of the vapor pressure of the pure solvent and the mole fraction of solvent.

**Raschig Process.** A method for production of phenol that begins with a firststage chlorination of benzene, using an air-hydrochloric acid mixture.

**Raschig Ring.** A type of packing in the shape of a short pipe; used in columns for absorption operations, and to a limited extent for distillation operations.

**Rast's Method.** A method of determining molecular weights by measuring the depression of freezing point of a solvent by a known weight of the solute whose molecular weight is required. Camphor is commonly used as the solvent because of its high molal depression constant. Molecular weights so determined are usually accurate to  $\pm 10\%$ ; the method is useful for determining  $E_n$  when the empirical formula  $E$  is known.

**Rat Distillate.** A refinery designation for gasoline and other fuels as they come from the condenser, before undesirable substances are removed by further processing.

**Raw Data.** A set of measurements made and recorded without regard to order, classification or suitable presentation is called raw data. The group of such measurements hardly reveals any meaning to the analytical chemist. Hence for a set of measurements to have any meaning or use, it is first of all arranged in an ascending order. Such an arranged data in order becomes information than being merely raw data. The minimum value, maximum value, number of scattered values, class frequency and frequency distribution make an analytical data to be easily understood. Hence classification of raw data is important in the representation of analytical results. Classification of data helps to (i) condense the large mass of data into a compact form, (ii) bring into prominence the significant features of the data and (iii) makes comparison easy. In other words, classification brings homogeneity to a diverse set of results.

First of all, the raw data available from a set of measurements is collected and then it is arranged in an order. The

minimum and the maximum values are identified. The spread or the range which is the difference between the maximum and minimum values is calculated. The values are then divided into different classes or cells. The number of observations that fall in each class or cell is called class frequency. A set of all distinct values of a measurement with their corresponding frequency is called frequency distribution. The frequency distribution is represented by frequency polygon or histogram.

**Rayleigh Line.** Spectrum line in scattered radiation which has the same frequency as the corresponding incident radiation.

**Reaction Enthalpy Number.** A dimensionless number used in the study of interphase transfer in chemical reactions, equal to the enthalpy of reaction per unit mass of a specified compound produced in a reaction, times the mass fraction of that compound, divided by the product of the specific heat at constant pressure and the temperature change during the reaction.

**Reactor.** Large-scale chemical processes are carried out in various environments, usually in tanks, tubes, towers or fluidized beds. These are usually referred to as chemical reactors and form the heart of the overall chemical process. Reactor design involving scale-up from laboratory reactions is an important aspect of chemical technology or chemical engineering. The term reactor is also used for a nuclear reactor.

**Reagent.** Any substance used in a reaction for the purpose of detecting, measuring, examining or analyzing other substances. High purity and high sensitivity are essential requirements of laboratory reagents. Over 8000 reagent chemicals are commercially available.

**Reagent Chemicals.** High-purity chemicals used for analytical reactions, for testing of new reactions where the effect of impurities are unknown, and, in general, for chemical work where impurities must either be absent or at a known concentration.

**Receiver.** Vessel, container, or tank used to receive and collect liquid material from a process unit, such as the distillate receiver from the overhead condenser of a distillation column.

**Reciprocating-plate Extractor.** A liquid-liquid contractor in which equally spaced perforated plates (as in a distillation column) move up and down rapidly over a short distance to cause liquid agitation and mixing. Also known as reciprocating-plate column.

**Recoil Ion Spectroscopy.** A method of studying highly ionized and highly excited atomic states, in which relatively light atoms in a gaseous target are bombarded by highly ionized, fast, heavy projectiles, resulting in single collisions in which the target atoms are raised to very high states of ionization and excitation while incurring relatively small recoil velocities.

**Recording Balance.** An analytical balance equipped to record weight results by electromagnetic or servomotor-driven accessories.

**Recrystallization.** The process of repeated crystallization carried out with the object to removing impurities or of obtaining more satisfactory crystals of a substance which is already pure.

**Rectification.** A method of separating a mixture into its components by fractional distillation of such importance that the terms rectification and fractional distillation are frequently used synonymously, despite the fact that two other methods are covered by the latter term. The process of rectification may be illustrated most readily by reference to the separation of a binary mixture into its components.

If a liquid mixture is brought into contact with a vapour containing less than the equilibrium amount of the lighter (*i.e.* more volatile) component, an exchange of material between phases will occur, some of the more volatile material entering the vapour and a corresponding quantity of the less volatile material entering the liquid phase. If the two phases are made to flow counter-current to each other over an extended path the lighter material will accumulate in the vapour phase and the heavier in the liquid phase. The longer the path the purer the two phases will become.

A rectifying or fractionating column consists of a long vertical cylinder containing either a series of plates, or a packing material having a large specific surface, both these arrangements ensuring good liquid-vapour contacting over the length of the unit. At the top of the column there is a condenser and at the bottom a vaporizing unit called a reboiler. The reboiler produces a stream of vapour which passes up the column to the condenser, where it is completely condensed and some of it is returned to the column as reflux. Due to the phenomenon of exchange between phases the liquid and vapour at the top consist almost entirely of the light component, and the material at the bottom of the heavy component.

Rectifying columns may be operated either batchwise or continuously. In the former case the vaporizer unit is a vessel (kettle) into which the charge of material to be fractionated is pure. As distillation proceeds the various component distil off in order of volatility, more or less sharp separations being achieved. In continuous operation the mixture is fed to the column at some point determined by its composition. Some of the liquid stream from the condenser is taken off continuously as overhead product (i.e. the light component), while the bottoms product, consisting of the heavy component, is drawn off via the reboiler. In the case of mixtures of more than two components, those of intermediate volatility accumulate at various points in the column from where they may be withdrawn.

The separating power of a rectifying column is dependent on the length of path over which vapour-liquid contacting can occur and the reflux ratio employed. The latter is the ratio of the quantity of liquid returned to the column as reflux to the quantity taken off as overhead product.

Rectification is of the greatest industrial importance; in particular, it is the principal separation process employed in the petroleum industry.

**Rectification Distillation.** A distillation technique in which a rectifying column is used.

**Rectifying Column.** Portion of a distillation column above the feed tray in which rising vapor is enriched by interaction with a countercurrent falling stream of condensed vapor; contrasted to the stripping column section below the column feed tray.

**Rectifying Column.** See rectification.

**Recuperators, Regenerators.** Heat-exchangers used in furnace operations where combustion air or lean fuel gas may be preheated. Recuperators are heat exchangers where heat is transferred from one flowing material to another, while regenerators are heat exchangers where heat is stored, with the heating and heated gases passing through the exchanger alternately.

**Recycle Mixing.** The mixing of a portion of a product stream (fluid or solid) from a processing unit with incoming raw feed.

**Redox.** Short form of the term oxidation-reduction, as in redox reactions, redox conditions, etc.

**Redox Potential.** Voltage difference at an inert electrode immersed in a reversible oxidation-reduction system; measurement of the state of oxidation of the system. Also known as oxidation-reduction potential.

**Redox Potentiometry.** Use of natural electrode probes to measure the solution potential developed as the result of an oxidation or reduction reaction.

**Redox System.** A chemical system in which reduction and oxidation (redox) reactions occur.

**Redox Titration.** A titration characterized by the transfer of electrons from one substance to another (from the reductant to the oxidant) with the end point determined colorimetrically or potentiometrically.

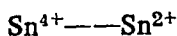
**Reducing Agent.** A material which brings about reduction and in the process is itself oxidized. Eg.  $\text{Sn}^{2+}$  reduces  $\text{Fe}^{3+}$  and is itself oxidized to  $\text{Sn}^{4+}$ .

**Reducing Atmosphere.** An atmosphere of hydrogen (or other substance that readily provides electrons) surrounding a chemical reaction or physical device; the effect is the opposite to that of an oxidizing atmosphere.

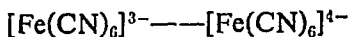
**Reducing Flame.** A flame having excess fuel and being capable of chemical reduction, such as extracting oxygen from a metallic oxide.

**Reducing Sugar.** Any of the sugars that because of their free or potentially free aldehyde or ketone groups, possess the property of readily reducing alkaline solutions of many metallic salts such as copper, silver, or bismuth; examples are the mono-saccharides and most of the disaccharide, including maltose and lactose.

**Reduction.** Chemical processes in which the proportion of electro-negative substituent is decreased, *e.g.*  $\text{FeCl}_3 \longrightarrow \text{FeCl}_2$ , or the charge on an ion is made more negative, *e.g.*



or



or the oxidation number is lowered. In organic chemistry the most obvious effect is to increase the proportion of hydrogen and to reduce the number of multiple bonds, *e.g.*  $\text{C}_2\text{H}_4$  (ethene)  $\longrightarrow$   $\text{C}_2\text{H}_6$  (ethane).

**Reduction Cell.** A vessel in which aqueous solutions of salts or fused salts are reduced electrolytically.

**Reduction Potential.** The potential drop involved in the reduction of a positively charged ion to a neutral form or to a less highly charged ion, or of a neutral atom to a negatively charged ion.

**Reference Electrode.** A nonpolarizable electrode that generates highly reproducible potentials; used for pH measurements and polarographic analysis; examples are the calomel electrode, silver-silver chloride electrode, and mercury pool.

**Reflectance Spectrophotometry.** Measurement of the ratio of spectral radiant flux reflected from a light-diffusing specimen to that reflected from a light-diffusing standard substituted for the specimen.

**Reflux.** In distillation processes in which a fractionating column is used, the term reflux refers to the liquid that has condensed from the rising vapor and allowed to flow back down the

column towards the still. As it does so, it comes into intimate contact with the rising vapor, resulting in improved separation of the components. The separation resulting from contact of the countercurrent streams of vapor and liquid is called rectification or fractionation.

**Reflux Condensor.** An auxiliary vessel for a distillation column that constantly condenses vapors and returns liquid to the column.

**Reflux Ratio.** The quantity of liquid reflux per unit quantity of product removed from the process unit, such as a distillation tower or extraction column.

**Refractometry.** Refractometry is regarded as simple physicochemical method of analysis. It requires very small amounts of the analyte and is performed during a very short time. In pharmaceutical analysis, it is used for identifying drugs, establishing their purity, and for quantitative determinations.

The refractometric method of analysis depends on measuring the refractive index of the analyte. The refractive index is one of the fundamental physical properties of a substance, namely, a pure substance is characterized by a definite refractive index. When a ray of light travels from one transparent medium into another one, its direction changes at the interface—the ray is refracted.

The ratio of the speed of light in the air ( $v_1$ ) to the speed of light in the substance being tested ( $v_2$ ), equal to the ratio of the sine of the angle of incidence of the light ray ( $\alpha$ ) to the sine of the angle of its refraction, ( $\beta$ ) is called the refractive index ( $n$ ) and is a constant for a given wavelength of the light ray :

$$n = \frac{v_1}{v_2} = \frac{\sin \alpha}{\sin \beta}$$

The value of the refractive index depends on the nature of a substance, the wavelength of the light, the concentration of the solution, and the temperature.

The refractive index is measured by a special instrument known as a refractometre.



The refractive index is customarily measured at 20°C and a wavelength of 589.3 nm of the sodium spectrum D line ( $n_D^{20}$ ).

The limits of measuring the refractive index in this case are 1.3 to 1.7.

**Regenerate.** To clean of impurities and make reusable as in regeneration of a catalytic cracking catalyst by burning off carbon residue, regeneration of clay adsorbent by washing free of adherents, or regeneration of a filtration system by cleaning off the filter media.

**Regenerator.** Device or system used to return a system or a component of it to full strength in a chemical process; examples are a furnace to burn carbon from a catalyst, a tower to wash impurities from clay, and a flush system to clean off the surface of filter media.

**Regnault's Method.** Obsolete method for determining gas densities by direct weighing of a known volume of gas under known conditions of temperature and pressure.

**Reid Vapour Pressure.** The vapour pressure of a petroleum product measured at a specific temperature (100°F) in an apparatus consisting of a chamber fitted with a pressure gauge.

**Reinecke's Salt, Ammonium Tetrathiocyanatodiamminechromate (III),**  $\text{NH}_4[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$ . Rose-coloured salt prepared from  $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$  and fused  $\text{NH}_4\text{NCS}$ . Forms sparingly soluble salts with organic bases used for the isolation of some amino-acids. Salts are known as reineckates.

**Reinsch Test.** A test for detecting small amounts of arsenic, silver, bismuth, and mercury.

**Relative Stability Test.** A color test using methylene blue that indicates when the oxygen present in a sewage plant's effluent or polluted water is exhausted.

**Remedial Operation.** In a chemical process operation, the revision of operating conditions so as to correct the overall operation and bring the product into desired rate or specification limits. Also known as corrective operation.

**Remote Handling Facilities.** Equipment used to carry out chemical reactions with intensely radioactive elements e.g. Am, or

to manipulate the very active fuel elements from a nuclear reactor.

**Rerunning.** The distillation of a liquid material that has already been distilled; usually implies taking a large proportion of the charge stock overhead.

**Residual Current.** When a current voltage curve is determined for a solution containing ions with a strongly negative reduction potential, a small current flows even before the decomposition of the solution begins. This current increases linearly with applied voltage and is due to charging of mercury drops due to applied voltage. The electrolyte in polarographic studies will also contain some traces of impurities which contribute to condenser current. Residual current consists of all such currents.

### **Residue**

1. The substance left after distilling off all but the heaviest components from crude oil in petroleum refinery operations. Also known as bottoms; residuum.
2. Solids deposited onto the filter medium during filtration. Also known as cake; discharged solids.

**Resin.** Any of a class of solid or semisolid organic products of natural or synthetic origin with no definite melting point, generally of high molecular weight; most resins are polymers.

**Resin-In-pulp Ion Exchange.** Combination of coarse anion-exchange resin with a slurry of finely ground uranium ore in an acid-leach liquor.

**Resinography.** Science of resins, polymers, plastics, and their products; includes study of morphology, structure, and other characteristics relatable to composition or treatment.

**Resolving Power.** The extent to which a lens can distinguish small particles and minute distances; *i.e.*, fine structure. The human eye can detect objects of about 1/250th inch (12.0 microns) in any dimension. The compound microscope has a resolving power of approximately 0.5 micron; an electron microscope can resolve fine structure as small as 5 Angstroms (5  $\times 10^{-10}$  m), that is,

in the molecular range. Two factors determine resolving power: the wavelength of the radiation utilized and the focal depth of the lens. The resolving power of a microscope is much more important than its ability to magnify, for no magnification, however large, can add detail to an image that was not first discerned by the lens system.

**Resonance Capture.** The combination of an incident particle and a nucleus in a resonance level of the resulting compound nucleus, characterized by having a large cross section at and very near the corresponding resonance energy.

#### **Resonance Fluorescence**

1. Resonant scattering from an atomic nucleus.
2. See resonance radiation.

**Resonance Ionization Spectroscopy.** A technique capable of detecting single atoms or molecules of a given element or compound in a gas, in which an atom or molecule in its ground state is excited to a bound state when a photon is absorbed from a laser beam at a very well-controlled wavelength that is resonant with the excitation energy; a second photon removes the excited electron from the atom or molecule, and this electron is then accelerated by an electric field and collides with the gas molecules, creating additional ionization which is detected by a proportional counter. Abbreviated RIS.

**Resonance Lamp.** An evacuated quartz bulb containing mercury, which acts as a source of radiation at the wavelength of the pure resonance line of mercury when irradiated by a mercury-arc lamp.

**Resonance Luminescence.** See resonance radiation.

**Resonance Radiation.** The emission of radiation by a gas or vapor as a result of excitation of atoms to higher energy levels by incident photons at the resonance frequency of the gas or vapor; the radiation is characteristic of the particular gas or vapor atom but is not necessarily the same frequency as the absorbed radiation. Also known as resonance fluorescence; resonance luminescence.

**Resonance Reaction.** A nuclear reaction that takes place only when the energy of the incident particles is at or very close to a characteristic value.

**Resonance Scattering.** A peak in the cross section of a nucleus for elastic scattering of neutrons at energies near a resonance level, accompanied by an anomalous phase shift in the scattered neutrons.

**Resonance Spectrum.** An emission spectrum resulting from illumination of a substance (usually a molecular gas) by radiation of a definite frequency or definite frequencies.

**Resonance Structure.** Any of two or more possible structures of the same compound that have identical geometry but different arrangements of their paired electrons; none of the structures has physical reality or adequately accounts for the properties of the compound, which exists as an intermediate form.

**Retention Index.** In gas chromatography, the relationship of retention volume with arbitrarily assigned numbers to the compound being analyzed; used to indicate the volume retention behavior during analysis.

**Retention Time.** In gas chromatography, the time at which the center, or maximum, of a symmetrical peak occurs on a gas chromatogram.

**Retention Volume.** In gas chromatography, the product of retention time and flow rate.

## Retort

1. A closed refractory chamber in which coal is carbonized for manufacture of coal gas.
2. A vessel for the distillation or decomposition of a substance.

**Retorting.** A process much used in the early years of chemistry for destructive distillation of heavy organic liquids and for laboratory separations. It involves the use of a cylindrical vessel made of glass (for laboratory work), fireclay or metal, with a neck bent at a downward angle to facilitate distillation. For gas manufacture the equipment is built on a heavier

in the molecular range. Two factors determine resolving power: the wavelength of the radiation utilized and the focal depth of the lens. The resolving power of a microscope is much more important than its ability to magnify, for no magnification, however large, can add detail to an image that was not first discerned by the lens system.

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**Retention Index.** In gas chromatography, the relationship of retention volume with arbitrarily assigned numbers to the compound being analyzed; used to indicate the volume retention behavior during analysis.

**Retention Time.** In gas chromatography, the time at which the center, or maximum, of a symmetrical peak occurs on a gas chromatogram.

**Retention Volume.** In gas chromatography, the product of retention time and flow rate.

### Retort

1. A closed refractory chamber in which coal is carbonized for manufacture of coal gas.
2. A vessel for the distillation or decomposition of a substance.

**Retorting.** A process much used in the early years of chemistry for destructive distillation of heavy organic liquids and for laboratory separations. It involves the use of a cylindrical vessel made of glass (for laboratory work), fireclay or metal, with a neck bent at a downward angle to facilitate distillation. For gas manufacture the equipment is built on a heavier

scale to handle destructive distillation of coal. Use of this term has been revived in current developments for processing shale oil.

**Reversal Spectrum.** A spectrum which may be observed in intense white light which has traversed luminous gas, in which there are dark lines where there were bright lines in the emission spectrum of the gas.

**Reverse Bonded-phase Chromatography.** A technique of bonded-phase chromatography in which the stationary phase is nonpolar and the mobile phase is polar.

**Reverse Deionization.** A process in which as ion-exchange unit and a cation-exchange unit are used in sequence to remove all ions from a solution.

**Reversed-phase Partition Chromatography.** Paper chromatography in which the low-polarity phase (such as paraffin, paraffin jelly, or grease) is put onto the support (paper) and the high-polarity phase (such as water, acids, or organic solvents) is allowed to flow over it.

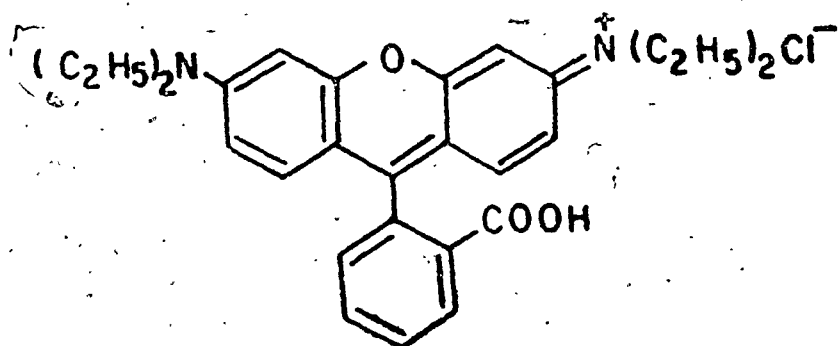
**Reverse Osmosis.** A technique used in desalination and waste-water treatment; pressure is applied to the surface of a saline (or waste) solution, forcing pure water to pass from the solution through a membrane (hollow fibres of cellulose acetate or nylon) that will not pass sodium or chloride ions.

**Reversible Electrode.** An electrode that owes its potential to unit charges of a reversible nature, in contrast to electrodes used in electroplating and destroyed during their use.

**Reynolds Analogy.** Relationship showing the similarity between the transfer of mass, heat, and momentum.

**Reynold Number.** A dimensionless number which is significant in the design of a model of any system in which the effect of viscosity is important in controlling the velocities or the flow pattern of a fluid; equal to the density of a fluid, times its velocity, times a characteristic length, divided by the fluid viscosity. Symbolized  $N_{Re}$ . Also known as Damkohler number  $V$  (DaV).

**Rhodamine B (or Tetraethyl-rhodamine) Reagent.** Antimony (V) salts



form violet benzene layer with the reagent. Thus the Sb(III) salts must be oxidized by adding  $\text{NaNO}_3$  in the presence of conc.  $\text{HCl}$  in the test solution.

**Test.** Place 5 drops of 1:3 dil.  $\text{H}_2\text{SO}_4$  in a semi-micro test tube and add one drop of the test solution. Now add 1 drop of 10 per cent  $\text{Kf}$  solution and 1 mL benzene, shake the solution well and take 2 drops of this solution on a spot plate. Add one drop of the reagent solution (0.2 per cent aqueous solution).

A violet benzene layer indicates antimony, the limit of identification being  $0.25 \mu\text{g. Sb}$ ; conc. limit, 1 in 100,000.

**Rice's Bromine Solution.** Analytical reagent for the quantitative analysis of urea; has 12.5% bromine and sodium bromide in aqueous solution.

**Riegler's Test.** Analytical technique for nitrous acid; uses sodium naphthionate and  $\beta$ -naphthol.

**Ring and Ball Softening Point.** A standard, empirical method for determination of the softening point of bitumen, tar or similar semi-solid material. The softening point is the temperature at which a disc of the material, contained in a metal ring, becomes soft enough to allow a standard steel ball placed on top of the disc, to fall a specified distance.

**Ring and Ball Test.** A test for determining the melting point of asphalt, waxes, and paraffins in which a small ring is fitted with a test sample upon which a small ball is then placed; the



melting point is that temperature at which the sample sufficiently to allow the ball to fall through the ring. Also known as ball and ring method.

**Ringer's Solution.** A solution of 0.86 gram sodium chloride, 0.03 gram potassium chloride, and 0.033 gram calcium chloride in boiled, purified water, used topically as a physiological salt solution.

**Ritter Reaction.** A procedure for the preparation of amides by reacting alkenes or tertiary alcohols with nitriles in an acidic medium.

**Ritz Formula.** A particular expansion of an equation used in studying the spectra of atoms.

**Ritz's Combination Principle.** The empirical rule that sums and differences of the frequencies of spectral lines often equal other observed frequencies. Also known as combination principle.

**Rotary-disk Contractor.** Liquid-liquid contactor, having a vertical cylindrical shell with vertical rotating shaft upon which are mounted a spaced series of flat disks : spinning of the disks forces liquid into spell-mounted baffles, causing mixing : used for liquid-liquid extraction processes. Also known as RDC extractor.

**Rotating-drum Heat Transfer.** Procedure for solidifying layers of solids onto the outside surface of an inside-cooled drum that is partly immersed in a melt of the solids material.

**Rotating Platinum Electrode.** Platinum wire sealed in a soft-glass tubing and rotated by a constant-speed motor; used as the electrode in amperometric titrations. Abbreviated RPE.

**Rotational Constant.** That constant proportioned to the moment of inertia of a linear molecule; used in calculations of microwave spectroscopy quantum.

**Rotational Energy.** For a diatomic molecule, the difference between the energy of the actual molecule and that of an idealized molecule which is obtained by the hypothetical process of gradually stopping the relative rotation of the nuclei without placing any new constraint on their vibration, or on motions of electrons.

**Rotational Level.** An energy level of diatomic molecule characterized by a particular value of the rotational energy and of the angular momentum associated with the motion of the nuclei.

**Rotational Quantum Number.** A quantum number  $J$  characterizing the angular momentum associated with the motion of the nuclei of a molecule; the angular momentum is  $(h/2\pi)\sqrt{J(J+1)}$  and the largest component is  $(h/2\pi)J$ , where  $h$  is Planck's constant.

**Rotational Spectrum.** When a molecule absorbs energy it may increase its total rotational energy as a whole (see band spectrum). Conversely, the transition from a state of higher to one of lower rotational energy corresponds to the emission of energy, which may be of light of frequency  $\nu$ ; the energy  $E$  emitted being given by  $E=h\nu$ . The lines in the molecular spectrum corresponding to such transitions are termed rotational bands, which are characteristic of molecule. Taken collectively the rotational bands comprise the rotational spectrum of the molecule. Rotational transitions are associated with lower energies than vibrational or electronic transitions, and hence the frequency of the emitted light is small. Rotational spectra are associated with the far i.r. and microwave regions of the electromagnetic spectrum.

**Rotational Sum Rule.** The rule that, for a molecule which behaves as a symmetric top, the sum of the line strengths corresponding to or from a given rotational level is proportional to the statistical weight of that level, that is, to  $2J+1$ , where  $J$  is the total angular momentum quantum number of the level.

**Rotational Transformation.** A type of crystal transformation that is a change from an ordered phase to a partially disordered phase by rotation of groups of atoms.

**Rotation Axis.** A symmetry element of certain crystals in which the crystal can be brought into a position physically indistinguishable from its original position by a rotation through an angle of  $360^\circ/n$  about the axis, where  $n$  is the multiplicity of the axis, equal to 2, 3, 4, or 6. Also known as symmetry axis.

**Rotation-inversion Axis.** A symmetry element of certain crystals in which a crystal can be brought into a position physically indistinguishable from its original position by a rotation through an angle of  $360^\circ/n$  about the axis followed by an inversion, where  $n$  is the multiplicity of the axis, equal to 1, 2, 3, 4, or 6. Also known as inversion axis.

**Rotation Spectrum.** Absorption-spectrum (absorbed electromagnetic energy) wavelengths produced if only the rotational energy of a molecule is affected during excitation.

**Rotation-vibration Spectrum.** Absorption-spectrum (absorbed electromagnetic energy) wavelengths produced when both the energy of vibration and energy of rotation of a molecule are affected by excitation.

**Rotatory Power.** The product of the specific rotation of element or compound and its atomic or molecular weight.

**Rowland Circle.** A circle drawn tangent to the face of a concave diffraction grating at its midpoint, having a diameter equal to the radius of curvature of a grating surface; the slit and camera grating should lie on the this circle.

**Rowland Ghost.** A false spectral line produced by a diffraction grating, arising from periodic errors in groove position.

**Rowland Mounting.** A mounting for a concave grating spectrograph in which camera and grating are connected by a bar forming a diameter of the Rowland circle, and the two run on perpendicular tracks with the slit placed at their junction.

**Rushton-Oldshue Column.** A mixing unit used for continuous pipeline blending in which two-phase contacting is desired; it is a column containing separation plates, baffles, and mixing impellers.

**Russell Movable-wall Oven.** An oven for carbonization which cokes a 400-pound (180-kilogram) charge in a horizontal, 12-inch-wide (30-centimeterwide) chamber, heated from both sides, but with one side floating and balanced against scales.

**Rutherford Backscattering Spectrometry.** A method of determining the concentrations of various elements as a function of depth

## Rydborg Series Formula

beneath the surface of a sample, by measuring the energy spectrum of ions which are backscattered out of a beam directed at the surface.

Ry. See rydberg.

## Rydberge

1. A unit of energy used in atomic physics, equal to the square of the charge of the electron divided by twice the Bohr radius; equal to  $13.60583 \pm 0.00004$  electronvolts. Symbolized ry.
2. See kayser.

**Rydberg Atom.** An atom whose outer electron has been excited to very high energy states, far from the nucleus.

## Rydberg Constant

1. An atomic constant which enters into the formulas for wave numbers of atomic spectra, equal to  $2\pi^2me^4/ch^3$ , where  $m$  and  $e$  are the rest mass and charge of the electron,  $c$  is the speed of light, and  $h$  is Planck's constant; equal to  $109,737.31 \pm 0.01$  inverse centimeters. Symbolized  $R_\infty$ .
2. For any atom, the Rydberg constant (first definition) divided by  $1+m/M$ , where  $m$  and  $M$  are the masses of an electron and of the nucleus.

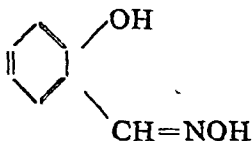
**Rydberg Correction.** A term inserted into a formula for the energy of a single electron in the outermost shell of an atom to take into account the failure of the inner electron shells to screen the nuclear charge completely.

**Rydberg Series Formula.** An empirical formula for the wave numbers of various lines of certain spectral series such as neutral hydrogen and alkali metals; it states that the wave number of the  $n$ th member of the series is  $\lambda x - R/(n+d)^2$ , where  $\lambda x$  is the series limit,  $R$  is the Rydberg constant of the atom, and  $a$  is an empirical constant.

# S

**Saddle-point Azeotrope.** A rarely occurring azeotrope which formed in ternary systems and for which the boiling point is intermediate between the highest and lowest boiling mixture in the system.

**Salicyldoxime :**



This is a reagent for  $\text{Ni}^{+2}$ ,  $\text{Pd}^{+2}$ ,  $\text{Cu}^{+2}$  for their participation under some selective conditions.

(Copper salts give a yellow-green ppt. with reagent in acetic acid solution.

**Test.** Take 2 drops of the test solution in a semi-micro test tube and slightly acidify it with acetic acid. Add 1 drop of the reagent solution (1 g reagent is dissolved in 5 mL ethanol and pour the solution dropwise into 95 mL of water; shake and filter. Use filtrate as a reagent solution).

A yellow-green ppt. indicates copper, the limit of identification being  $0.5 \mu\text{g Cu}$ ; conc. limit, 1 in 100,000.

**Salt Bridge.** A bridge of a salt solution, usually potassium chloride, placed between the two half-cells of a galvanic cell, either to reduce to a minimum the potential of the liquid junction between the solutions of the two half-cells or to isolate a solution under study from a reference half-cell and prevent chemical precipitations.

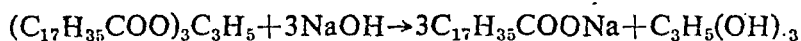
**Salt Error.** An error introduced in an analytical determination of a saline liquid such as sea water; caused by the effect of the neutral ions in the solution on the color of the pH indicator, and hence upon the apparent pH.

**Salt Grainer.** Type of evaporative crystallizer in which the solution is kept hot, and supersaturation is developed by evaporation rather than by cooling.

**Salting-out Effect.** The growth of crystals of a substance on heated, liquid-holding surfaces of a crystallizing evaporator as a result of the decrease in solubility of the substance with increase in temperature.

**Sampling.** The methods and the techniques used in obtaining representative test samples of quantity lots of raw materials, semiprocessed work, and finished product for production and quality control. Rules for sampling procedures for both solid and liquid materials have been established by the National Cottonseed Products Association, Memphis, Tenn., and by the National Institute of Oilseed Products, San Francisco, Cal. The techniques of physical sampling are one application of statistical quality control.

**Saponification.** The chemical reaction in which an ester is heated with aqueous alkali such as sodium hydroxide, to form an alcohol (usually glycerol), and the sodium salt of the acid corresponding to the ester. The process is usually carried out on fact, (glyceryl esters of fatty acids). The sodium salt formed is called a soap (q.v.). A typical saponification reaction is :



**Saponification.** The process of converting chemicals into soap; involves the alkaline hydrolysis of a fat or oil, or the neutralization of a fatty acid.

**Saponification Equivalent.** The quantity of fat in grams that can be saponified by 1 liter of normal alkalies.

**Saponification Number.** Milligrams of potassium hydroxide required to saponify the fat, oil, or wax in a 1-gram sample of a given material, using a specific ASTM test method.

**Saponification Value.** The saponification value of a fat is the number of mg of KOH neutralized during saponification of one g of the fat. It is a measure of the mean mol.wt. of the fatty acids in the fat molecule. Fats such as lard give values

about 195, whereas butter and other fats with a high proportion of the lower fatty acids have values about 225-230.

**Satellite Infrared Spectrometer.** A spectrometer carried aboard satellites in the Nimbus series which measures the radiation from carbon dioxide in the atmosphere at several different wavelengths in the infrared region, giving the vertical temperature structure of the atmosphere over a large part of the earth. Abbreviated SIRS.

**Saturated Interference Spectroscopy.** A version of saturation spectroscopy in which the gas sample is placed inside an interferometer that splits a probe laser beam into parallel components in such a way that they cancel on recombination; intensity changes in the recombined probe beam resulting from changes in absorption or refractive index induced by a laser saturating beam are then measured.

**Saturation Spectroscopy.** A branch of spectroscopy in which the intense, monochromatic beam produced by a laser is used to alter the energy-level populations of a resonant medium over a narrow range of particle velocities, giving rise to extremely narrow spectral lines that are free from Doppler broadening; used to study atomic, molecular, and nuclear structure, and to establish accurate values for fundamental physical constants

**Scattering Length:** A parameter used in analyzing nuclear scattering at low energies; at the energy of the bombarding particle becomes very small, the scattering cross section approaches that of an impenetrable sphere whose radius equals this length. Also known as scattering power.

**Scattering Plane.** In a quasielastic light-scattering experiment performed with the use of polarizers, the plane containing the incident and scattered beams.

**Scattering Power.** See scattering length.

**Scheible Extractor.** Liquid-liquid contact vessel used in liquid-liquid extraction processes: a vertical cylinder with interspersed open spaces and wire-mesh packing along its height, with liquid agitators in the open spaces, or a vertical cylinder

fully filled with wire-mesh packing. Also known as Scheibel column; Scheibel-York extractor; York-Scheibel column.

**Schiff Base.**  $RR'C=NR''$  Any of a class of derivatives of the condensation of aldehydes or ketones with primary amines; colorless crystals, weakly basic; hydrolyzed by water and strong acids to form carbonyl compounds and amines; used as chemical intermediates and perfume bases, in dyes and rubber accelerators, and in liquid crystals for electronics.

**Schiffs Reagent.** An aqueous solution of rosaniline and sulfurous acid; used in the Schiff test.

**Schiff Test.** A test for aldehydes by using an aqueous solution of rosaniline and sulfurous acid.

**Schmidt Lines.** Two lines, on a graph of nuclear magnetic moment versus nuclear spin, on which points describing all nuclides should lie, according to the independent particle model; experimentally, however, points describing nuclides are scattered between the lines.

**Schmidt Number 2.** See Semenov number 1.

**Schmidt Number 3.** A dimensionless number used in electrochemistry, equal to the product of the dielectric susceptibility and the dynamic viscosity of a fluid divided by the product of the fluid density, electrical conductivity, and the square of a characteristic length. Symbolized  $Sc_3$ .

**Schulze's Reagent.** An oxidizing mixture consisting of a saturated aqueous solution of  $KClO_3$  and varying amounts of concentrated  $HNO_3$ ; commonly used in palynologic macerations.

**Schuster Method.** A method for focusing a prism spectroscope without using a distant object or a Gauss eyepiece.

**Schweizer's Reagent.** The dark blue solution obtained by dissolving  $Cu(OH)_2$  in concentrated ammonia solution. Used as a solvent for cellulose, the cellulose, is precipitated on acidification. Used in the cuprammonium process for the manufacture of rayon.

**Scintillation Counter.** A device used to detect pulses of radiation by emitting a flicker of light. Gamma radiation is counted by



inorganic detectors such as sodium iodide, while organic materials such as plastics may be used for beta and alpha particles.

**Scraped-surface Exchanger.** A liquid-liquid heat-exchange device that has a rotating element with spring-loaded scraper blades to wipe the process-fluid exchange surfaces clean of crystals or other foulants; used in paraffin-wax processing.

**Screening.** Separation of solid material into fractions containing particles whose sizes lie within a certain range, by the use of sieves.

In all screening equipment separation is effected by passing the feed through a wire cloth, metal grid, perforated plate or other arrangement such that undersize passes through and oversize is retained on the screening surface. Industrial screens are normally shaken or vibrated.

**Scrubbers** These remove impurity from a gas by washing it with a liquid; the impurity may either be another gas or particles of suspended solid or liquid. In both cases the object is to ensure intimate contact between the two phases, and scrubbing equipment is therefore generally similar to gas absorption equipment.

**Second Boiling Point.** In certain mixtures, the temperature at which a gas phase develops from a liquid phase upon cooling.

**Sedimentation Balance.** A device to measure and record the weight of sediment (solid particles settled out of a liquid) versus time; used to determine particle sizes of fine solids.

**Sedimentation Coefficient.** In the sedimentation of molecules in an accelerating field, such as that of a centrifuge, the velocity of the boundary between the solution containing the molecules and the solvent divided by the accelerating field. (In the case of a centrifuge, the accelerating field equals the distance of the boundary from the axis of rotation multiplied by the square of the angular velocity in radians per second.)

**Sedimentation Constant.** A quantity used in studying the behavior of colloidal particles subject to forces, especially centrifugal forces; it is equal to  $2r^2(p-p')/9\eta$ , where  $r$  is the particle's

radius,  $p$  and  $p'$  are reciprocals of partial specific volumes of particle and medium respectively, and  $\eta$  is the medium's viscosity.

**Sedimentation Equilibrium.** The equilibrium between the forward movement of a sample's liquid-sediment boundary and reverse diffusion during centrifugation; used in molecular-weight determinations.

**Sedimentation Velocity.** The rate of movement of the liquid-sediment boundary in the sample holder during centrifugation; used in molecular-weight determinations.

**Seed Crystals.** Crystals which are added to a supersaturated solution to facilitate crystallization of the whole.

**Seger Cones.** Pyramids used in estimating the refractoriness of materials and as approximate measures of temperature in kilns and ovens. The cones function by bending on heating.

**Selective Adsorbent.** Material that will selectively adsorb (or reject) one or more specific components from a multicomponent mixture of gases or liquids; common adsorbents are silica gel, carbon and activated carbon, activated alumina, and synthetic or natural zeolites (molecular sieves).

**Selective Solubility Diffusion.** The transmission of fluids through a nonporous, polymeric barrier (membrane) by an adsorption-solution-diffusion-desorption sequence.

**Selective Solvent.** A solvent that, at certain temperatures and ratios with other materials, preferentially dissolves more of one component of a liquid or solids mixture than of another, thereby permitting partial separation.

**Selectivity Diagram** A triangular plot of solubilities in a ternary liquid system; used to calculate the ability of a solvent to extract a component from a mixture (its selectivity) at various concentration combinations.

**Selenoxide** A group of organic selenium compounds with the general formula  $R_2SeO$ .

**Seliwanoff's Test.** A color test helpful in the identification of ketoses, which develop a red color with resorcinol in hydrochloric acid.

**Semicarbazide Hydrochloride.**  $\text{CH}_5\text{ON}_3\cdot\text{HCl}$ . Colorless prisms, soluble in water, decomposing at  $175^\circ\text{C}$ ; used as an analytical reagent for aldehydes and ketones, and to recover constituents of essential oils. Also known as aminourea hydrochloride; carbamylhydrazine hydrochloride.

**Semicarbazone.**  $\text{R}_2\text{C}:\text{N}_2\text{HCOH}_2$ . A condensation product of an aldehyde or ketone with semicarbazide.

**Semimicroanalysis.** A chemical analysis procedure in which the weight of the sample is between 10 and 100 milligrams.

**Semimicrochemistry.** Any chemical method (usually analytical) in which the weight of the sample used is from 10 to 100 mg.

**Sensing Zone Technique.** Particle-size measurement in a dilute solution; with fine particles passed through a small zone (opening) so that individual particles may be observed and measured by electrolytic, photic, or sonic methods.

**Separating Power.** The measure of the ability of a system (such as a rectifying system) to separate the components of a mixture, when the components have increasingly close boiling points.

**Separation Energy.** The energy needed to remove a proton, neutron, or alpha particle from a nucleus.

**Separatory Funnel.** A funnel-shaped device used for the careful and accurate separation of two immiscible liquids; a stopcock on the funnel stem controls the rate and amount of outflow of the lower liquid.

**Sequestering Agent.** A substance that removes a metal ion from a solution system by forming a complex ion that does not have the chemical reactions of the ion that is removed; can be a chelating or a complexing agent.

**Series of Lines.** A collection of spectral lines of an atom or ion for a set of transitions, with the same selection rules, to a single final state; often the frequencies have a general formula of the form  $[\text{R}/(\text{a} + \text{c}_1)^2] - [\text{R}/(\text{n} + \text{c}_2)^2]$ , where R is the Rydberg constant for the atom, a and  $\text{c}_1$  and  $\text{c}_2$  are constants, and n takes on the values of the integers greater than a for the various lines in the series.

**Setting Point.** The temperature at which molten paraffin wax, when allowed to cool under standard conditions, first shows a rate of temperature change of 0.2K per minute.

**Severity Factor.** A measure of the severeness or intensity of overall reaction conditions in a chemical reaction; for example, the temperature, pressure, or conversion in a catalytic cracker or reformer.

**Sharp Series.** A series occurring in the line spectra of many atoms and ions with one, two, or three electrons in the outer shell, in which the total orbital angular momentum quantum number changes from 0 to 1.

**Shift of Spectral Line.** A small change in the position of a spectral line that is due to a corresponding change in frequency which, in turn, results from one or more of several causes, such as the Doppler effect.

**Short-tube Vertical Evaporator.** A liquid evaporation process unit with a vertical bundle of tubes 2—3 inches (5—8 centimeters) in diameter and 4—6 feet (1.2—1.8 meters) long; the heating fluid is inside the tubes, and the liquid to be evaporated is in the shell area outside the tubes; used mainly to evaporate cane-sugar juice. Also known as calandria evaporator; Roberts evaporator; standard evaporator.

**Sidestream Stripper.** A device used to perform further distillation on a liquid stream (sidestream) from one any of the plates of a bubble tower, usually with the use of steam.

**Sieve Plate, Sieve Tray.** This vapour-liquid contacting device, widely used in distillation and absorption columns, consists of a plate perforated by a large number of closely spaced holes 3-12mm in diameter. Vapour passing up through the holes is broken up into streams of bubbles which rise through the liquid on the plate. Like the bubblecap plate it is equipped with inlets and outlet weirs, and liquid passes from one plate to the next through downcomers. The sieve plate has become popular because it enjoys most of the advantages of the bubble-cap plate, but is considerably cheaper.

**Sieve Shaker.** A device used to shake a stacked column of standard sieve-test trays to cause solids to shift progressively from the

top (large openings) to the bottom (small openings and a final pan), according to particle size.

**Sieve Tray.** See sieve plate.

**Significant Figures.** To indicate the accuracy of a measurement, significant figures or significant digits are used. Significant figures are those digits which are exactly known and one digit of which there is an uncertainty. The position of the decimal points is irrelevant. Zero's are significant when they are part of the numbers but are insignificant when they represent the magnitude.

For example, the numbers 12045 or 120.45 or 0.12045 or 1204.5—all have five significant figures but for the number 8.314 0000 has only four significant figures as the zeroes represents only the magnitude and the zeroes become significant if the value is known with certainty.

**Silver Nitrate.**  $\text{AgNO}_3$ . Poisonous, corrosive, colorless crystals; soluble in glycerol, water, and hot alcohol; melts at  $212^\circ\text{C}$ ; used in external medicine, photography, hair dyeing, silver plating, ink manufacture, and mirror silvering, and as a chemical reagent.

**Single-effect Evaporation.** An evaporation process completed entirely in one vessel or by means of a single heating unit.

**Sliding-vane Compressor.** A rotary-element gas compressor in which spring-loaded sliding vanes (evenly spaced around a cylinder off-center in a surrounding chamber) pick up, compress, and discharge gas as the cylinder revolves.

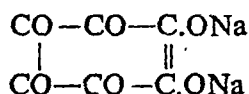
**Slipband.** One of the microscopic parallel lines (Luders' lines) on the surface of a crystalline material stretched beyond its elastic limit, located at the intersection of the surface with intracrystalline slip planes in the grains of the material. Also known as slip line.

**Sodium Bismulthate.**  $\text{NaBiO}_3$ .

Properties: Yellow or brown, amorphous powder. Slightly hygroscopic. Insoluble in cold water; decomposes in hot water and acids. Low toxicity.

Uses : Analysis (testing for manganese in iron, steel and ores); reagent; pharmaceuticals.

### Sodium Rhodizonate Reagent



Barium salts give red-brown colour with the reagent. The interference is due to Fe, Pb, Sr and  $\text{S}^{2-}$ . These ions must be removed before the test is applied, but  $\text{Sr}^{2+}$  can be distinguished from  $\text{Ba}^{2+}$  by exposing the red-brown spot to HCl fumes, the colour of the spot will be discharged if it was produced by  $\text{Sr}^{2+}$ .

Test. Place 1 drop of the test solution (neutral or very slightly acidic) and one drop of the reagent solution (freshly prepared 0.2 per cent aqueous solution) on a filter paper. Expose the filter paper to ammonia fumes.

A red-brown colour indicates barium, the limit of identification being 0.25  $\mu\text{g}$  Ba; conc. limit, 1 in 200,000.

**Sodium Rhodizonate Reagent.** In the absence of  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  and  $\text{Pb}^{2+}$ ,  $\text{Ca}^{2+}$  may be detected by means of the reagent.

Test. Place 1 drop of the test solution (neutral or weakly acidic) on a spot plate. Add 1 drop of the reagent solution (freshly prepared 0.2% aqueous solution). Now add 1 drop of 0.5 N NaOH solution and mix.

A violet ppt. indicates calcium, the limit of identification being 1  $\mu\text{g}$  Ca.

**Soft Water.** Water that is free of magnesium or calcium salts.

**Soft X-ray Absorption Spectroscopy.** A spectroscopic technique which is used to get information about unoccupied states above the Fermi level in a metal or about empty conduction bands in an inoculator.

**Soft X-ray Appearance Potential Spectroscopy.** A branch of electron spectroscopy in which a solid surface is bombarded with monochromatic electrons, and small but abrupt changes in the resulting total x-ray emission intensity are detected as the energy of the electrons is varied. Abbreviated SXAPS.

**Soll Chemistry.** The study and analysis of the inorganic and organic components and the life cycles within soils.

**Sol.** A colloidal solution consisting of a suitable dispersion medium, which may be gas, liquid, or solid, and the colloidal substance, the disperse phase, which is distributed throughout the dispersion medium.

**Solar Distillation.** A procedure in which the sun's heat is used to evaporate sea-water in order to produce sodium chloride and other salts or potable water.

**Solar Still.** A device for evaporating seawater, in which water is confined in one or more shallow pools, over which is placed a roof-shaped transparent cover made of glass or plastic film; the sun's heat evaporates the water, leaving behind a residue of salt; the vapor from the evaporated water condenses on the surface of the cover and trickles down into gutters, which thus collect fresh water.

**Solid-phase Synthesis.** A term applied to the technique of carrying out chemical transformations on a substrate chemically bonded to an insoluble, solid polymer molecule. R. B. Merrifield has developed this technique with considerable success for the synthesis of polypeptides from amino-acids using another amino-acid bonded to a polystyrene matrix. The advantage is that the products at each stage of a multi-step synthesis need not be isolated and purified. Instead the polymer to which the peptide is attached is washed free of excess reagents and impurities and virtually no loss of product occurs. The method has been adapted to automatic control and addition of reagents. At the completion of the desired synthesis the product is liberated from the polymer surface by a suitable reagent.

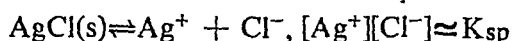
**Solubility.** Solubility is defined as the concentration of a particular ion forming the salt. For example the solubility product

$$K_{sp} \text{ of } AgCl = [Ag^+][Cl^-]$$

$$= [Ag^+] = [Cl^-]$$

$$\therefore \text{Solubility of } AgCl = \sqrt{K_{sp}} = [Ag^+] = [Cl^-]$$

**Solubility Product Constant.** A type of simplified equilibrium constant,  $K_{sp}$ , defined for and useful for equilibria between solids and their respective ions in solution; for example, the equilibrium



where  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  are molar concentrations of silver ions and chloride ions.

### **Solubility Test**

1. A test for the degree of solubility of asphalts and other bituminous materials in solvents, such as carbon tetrachloride, carbon disulfide, or petroleum ether.
2. Any test made to show the solubility of one material in another (such as liquid-liquid, solid-liquid, gas-liquid, or solid-solid).

**Solution.** A single, homogeneous liquid, solid, or gas phase that is a mixture in which the components (liquid, gas, solid, or combinations thereof) are uniformly distributed throughout the mixture.

### **Solution Pressure**

1. A measure of the tendency of molecules or atoms to cross a bounding surface between phases and to enter into a solution.
2. A measure of the tendency of hydrogen, metals, and certain nonmetals to pass into solution as ions.

**Solution Process.** An oil-refining process for separating mercaptans from gasoline by washing with a caustic solution containing organic compounds in which the mercaptans are soluble.

**Solutizer-air Regenerative Process.** A petroleum refinery process that is identical to the solutizer-steam regeneration process, except for the regeneration step; the newer units use uncatalyzed air regeneration.

**Solutizer-steam Regenerative Process.** A petroleum refinery process used to extract mercaptans from gasoline or naphtha; uses solutizers (potassium isobutyrate or potassium alkyl phenolate) in strong potassium hydroxide solution as the selective solvent.



**Solutizer-tannin Process.** A petroleum refinery process that is an early variation of the solutizer-air regenerative process for extraction of mercaptans from gasoline; uses tannin-catalyzed oxidation for the regeneration step.

**Solvent Drying.** Removal of water from metal surfaces by means of a solvent that displaces it preferentially as on precision equipment, electronic components etc. Examples of solvents used are acetone, 1,1,2-trichloro-1,2,2-trifluoroethane, 1,1,1-trichloroethane.

**Solvent Extraction.** A separation operation which may involve three types of mixtures: (a) a mixture composed of two or more solids, such as a metallic ore; (b) a mixture composed of a solid and a liquid, (c) a mixture of two or more liquids. One or more components of such mixtures are removed (extracted) by exposing the mixture to the action of a solvent in which the component to be removed is soluble. If the mixture consists of two or more solids, extraction is performed by percolation of an appropriate solvent through it. This procedure is also called leaching, especially if the solvent is water coffee-making is an example. Synthetic fuels can be made from coal by extraction with a coal-derived solvent followed by hydrogenation.

In liquid-liquid extraction one or more components are removed from a liquid mixture by intimate contact with a second liquid which is itself nearly insoluble in the first liquid and dissolves the impurities and not the substance that is to be purified. In other cases the second liquid may dissolve, *i.e.* extract, from the first liquid, the component that is to be purified, and leave associated impurities in the first liquid. Liquid-liquid extraction may be carried out by simply mixing the two liquids with agitation, and then allowing them to separate by standing. It is often economical to use counter-current extraction, in which the two immiscible liquids are caused to flow past or through one another in opposite directions. Thus fine droplets of heavier liquid can be caused to pass downward through the lighter liquid in a vertical tube or tower.

The solvents used vary with the nature of the products involved. Widely used are water, hexane, acetone, isopropyl alcohol, furfural, xylene, liquid sulfur dioxide, and tributyl phosphate. Solvent extraction is an important method of both producing and purifying such products as lubricating and vegetable oils, pharmaceuticals, and nonferrous metals.

Solvent extraction is a method of separation based on the distribution of a substance between two immiscible liquids. Generally an aqueous solution of a substance is brought into contact with another solvent (usually organic) such that distribution of solute takes place between the two liquids. The extraction of a solute in a particular solvent can be represented by the term, distribution coefficient  $D$ .

$$\text{The distribution coefficient } D = \frac{C_o}{C_w}$$
$$= \frac{\text{Conc. of solute in org. Phase}}{\text{Conc. of solute in aqu. Phase}}$$

There are three different types of solvent extraction. They are :

- (1) Batch extraction,
- (2) Continuous extraction,
- (3) Countercurrent extraction.

(1) Batch extraction : This is a simple method of extraction using a separating funnel. The method is applicable for substances with high distribution coefficients. In this method an aqueous solution containing the solute is mixed with suitable org. solvent and a thorough mixing of the two solutions is done by shaking. After equilibrium, the two immiscible layers separate out, from which the separation of two liquids can be achieved. For org. solvents of less density like benzene, the org. layer will be the upper layer and in such cases, a suitable modified separating funnel will be used. By using Hg, the level of org. layer is increased which can be collected by using the modified separating funnel.

(2) Continuous extraction : Continuous extraction was

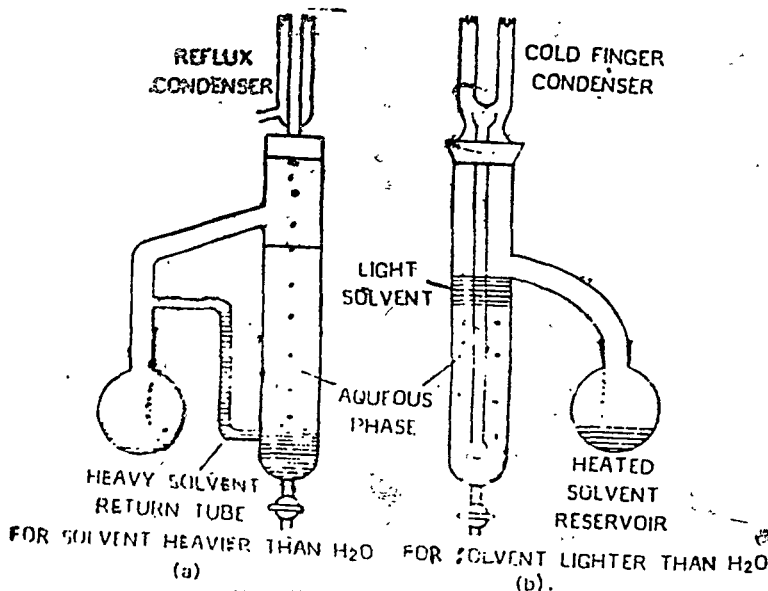


Fig. 6

devised by Kutcher and Steudel. This method of extraction is also applicable to different types of organic solvents. In this a portion of the extracting solvent is placed in a heated reservoir. The vapours of the solvent pass through the condenser and in doing so, the solvent carries some solute and the extracting solvent then overflows into the heated reservoir. By doing this, the solute is continuously extracted by the solvent and accumulates in the reservoir.

(3) Counter Current Extraction : Counter current extraction is used when the solutes to be extracted have small differences in their distribution ratios. It is a multiple distribution process with a large number of stages. Craig and Post devised an all glass apparatus which is usually called a Craig counter current extractor. It consists of many separating chambers and in each chamber distribution of solutes occurs. Depending on the rate of distribution, the components of a sample distribute at different speed in different chamber, leading to separation of constituents. The extracting solvent

and the solution containing the solutes are introduced through A to B and after attaining equilibrium the chamber is fitted

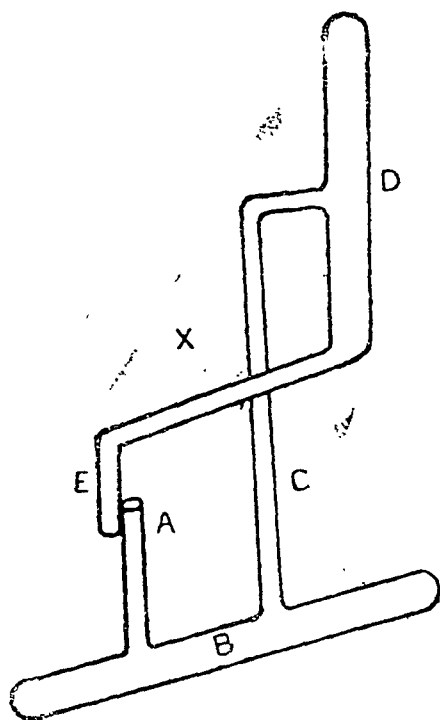


Fig. 7

such that the higher phase travels through C to D from which it comes to another equilibrium chamber through E. The different solutes present in the solution are collected in this way in different chambers.

**Solvent Recovery.** For reuse purposes, the catching and recovery of solvent vapors from vent lines, process vessels, or other sources of evaporative loss, usually with a solid adsorbent material.

**Solvent-refined.** Pertaining to any product material whose final quality and condition is in part the result of a solvent treatment during processing of the feedstock material.

**Solvent Refining.** The process of treating a mixed material with a solvent that preferentially dissolves and removes certain minor constituents (usually the undesired ones); common in the petroleum refining industry.

**Solvolysis.** A reaction in which a solvent reacts with the solute to form a new substance.

**Sommelet Process.** The preparation of thiophene aldehydes by treatment of thiophene with hexamethylenetetramine.

**Sommerfeld Law for Doublets.** According to the Bohr-Sommerfeld theory, the splitting in frequency of regular or relativistic doublets is  $\alpha^2 R(Z - \sigma)^4 / n^3(l + 1)$ , where  $\alpha$  is the fine structure constant,  $R$  is the Rydberg constant of the atom,  $Z$  is the atomic number,  $\sigma$  is a screening constant,  $n$  is the principal quantum number, and  $l$  is the orbital angular momentum quantum number.

**Sonnenschein's Reagent.** A solution of phosphomolybdic acid that forms a yellow precipitate with alkaloid sulfates.

**Sorensen Titration.** Titration with one of the Sorensen hydrogen-ion-concentration indicators.

**Soxhlet Extractor.** A laboratory apparatus consisting of a glass flask and condensing unit used for continuous reflux extraction of alcohol-or ether-soluble components of food products. Named after its inventor, a German chemist.

**Soxhlet Extractor.** A flask and condenser device for the continuous extraction of alcohol-or ether-soluble materials.

**Space Group Extinction.** The absence of certain classes of reflections in the x-ray diffraction pattern of a crystal due to the existence of symmetry elements in the space group of the crystal which are not present in its point group.

**Space Velocity.** The relationship between feed rate and reactor volume in a flow process; defined as the volume or weight of feed (measured at standard conditions) per unit time per unit volume of reactor (or per unit weight of catalyst).

**Spallation Reaction.** A high-energy nuclear reaction which results in the release of large numbers of nucleons as reaction products.

**Spark Excitation.** The use of an electric spark (10,000 to 30,000 volts) to excite spectral line emission from otherwise hard-to-excite samples; used in emission spectroscopy.

- Spark Explosion Method.** A technique for the analysis of hydrogen; the sample is mixed with an oxidant and exploded by a spark or hot wire, and the combustion products are then analyzed.
- Spark Spectrum.** The spectrum produced by a spark discharging through a gas or vapor; with metal electrodes, a spectrum of the metallic vapor is obtained.
- Specification.** A schedule of minimum performance requirements for specialized products, such as those established by the various committees of the American Society for Testing and Materials and the Underwriters Laboratories. Such products are subject to inspection and test before acceptance.
- Specific Mass Shift.** The portion of the mass shift that is produced by the correlated motion or different pairs of atomic electrons and is therefore absent in one-electron systems.
- Specific Retention Volume.** The relationship among retention volume, void volume, and adsorbent weight, used to standardize gas chromatography adsorbents by the elution of a standard solute by a standard eluent from the adsorbent under test.
- Specific Susceptibility.** See mass susceptibility.
- Spectral Bandwidth.** The minimum radiant-energy bandwidth to which a spectrophotometer is accurate; that is, 1—5 nanometers for better models.
- Spectral Directional Reflectance Factor.** In spectrophotometric colorimetry, the ratio of the energy diffused in any desired direction by the object under analysis to that energy diffused in the same direction by an ideal perfect (energy) diffuser.
- Spectral Line.** A discrete value of a quantity, such as frequency, wavelength, energy, or mass, whose spectrum is being investigated; one may observe a finite spread of values resulting from such factors as level width, Doppler broadening, and instrument imperfections. Also known as spectrum line.
- Spectral Radiance Factor.** A situation when the desired direction for analysis of energy diffused from (reflected from) an object under spectrophotometric colorimetric analysis are a

substantially the same (a solid angle of nearly zero steradians).

**Special Reflectance.** Situation when the desired directions for analysis of energy from (reflected from) an object under spectrophotometric colorimetric analysis is diffused in all directions (not directed as a single beam).

**Spectral Regions.** Arbitrary ranges of wavelength, some of them overlapping, into which the electromagnetic spectrum is divided, according to the types of sources that are required to produce and detect the various wavelengths, such as x-ray, ultraviolet, visible, infrared, or radio-frequency.

**Spectral Sensitization.** The process by which the natural sensitivity of a photographic silver halide emulsion is extended to light of longer wavelength by means of sensitizing dyes. Using appropriate sensitizers, orthochromatic and i.r. sensitive emulsions are produced. For colour photography, tri-pack materials incorporate three sensitive layers sensitized to red, green and blue light.

**Spectral Sensitizers.** Dyes which extend the sensitivity of silver halide emulsions to light of wave-lengths beyond the region of natural sensitivity of silver halide. Essential properties for sensitizers include intense light absorption in the appropriate region, powerful adsorption to the grain surface and the ability to transfer the absorbed energy to the conduction band of the crystal. Structurally, the majority of sensitizers are polymethine dyes, e.g. cyanines.

**Spectral Series.** Spectral lines or groups of lines that occur in sequence.

**Spectrobolometer.** An instrument that measures radiation from stars; measurement can be made in a narrow band of wave-lengths in the electromagnetic spectrum; the instrument itself is a combination spectrometer and bolometer.

**Spectrofluorometer.** A device used in fluorescence spectroscopy to increase the selectivity of fluorometry by passing emitted fluorescent light through a monochromator to record the fluorescence emission spectrum.

**Spectrogram.** The record of a spectrum produced by a spectrograph.

**Spectrograph.** A spectroscope provided with a photographic camera or other device for recording the spectrum.

**Spectrography.** The use of photography to record the electromagnetic spectrum displayed in a spectroscope.

**Spectrometer**

1. A spectroscope that is provided with a calibrated scale either for measurement of wavelength or for measurement of refractive indices of transparent prism materials.
2. A spectroscope equipped with a photoelectric photometer to measure radiant intensities at various wavelengths.

**Spectrometry.** The use of spectrographic techniques for deriving the physical constants of materials.

**Spectrophone.** A cell containing the sample in the optoacoustic detection method; equipped with windows through which the laser beam enters the cell and a microphone for detecting sound.

**Spectrophotometer.** An instrument that measures (often automatically) the relation between absorption of electromagnetic radiation and frequency of that radiation (or wavelength). Spectrophotometers operate in various regions of the electromagnetic spectrum, *e.g.* u.v., visible, i.r., microwave.

**Spectrophotometric Titration.** An analytical method in which the radiant-energy absorption of a solution is measured spectrophotometrically after each increment of titrant is added.

**Spectrophotometry.** A procedure to measure photometrically the wavelength range of radiant energy absorbed by a sample under analysis; can be by visible light, ultraviolet light, or x-rays.

**Spectropyrhellometer.** An astronomical instrument used to measure distribution of radiant energy from the sun in the ultraviolet and visible wavelengths.

**Spectroscope.** An optical instrument consisting of a slit, collimator



lens, prism or grating, and a telescope or objective lens which produces a spectrum for visual observation.

**Spectroscopic Displacement Law.** The spectrum of an un-ionized atom resembles that of a singly ionized atom of the element one place higher in the periodic table, and that of a doubly ionized atom two places higher in the table, and so forth.

**Spectroscopic Splitting Factor.** See Lande  $g$  factor.

**Spectroscopy.** (instrumental analysis). A branch of analytical chemistry devoted to identification of elements and elucidation of atomic and molecular structure by measurement of the radiant energy absorbed or emitted by a substance in any of the wavelengths of the electromagnetic spectrum in response to excitation by an external energy source. The types of absorption and emission spectroscopy are usually identified by the wavelength involved, namely, gamma ray, x-ray, ultraviolet, visible, infrared, microwave and radiofrequency. The technique of spectroscopic analysis was originated by Fraunhofer who in 1814 discovered certain dark (D) lines in the solar spectrum, which were later identified as characterizing the element sodium. In 1861 Kirchhoff and Bunsen produced emission spectra and showed their relationship to Fraunhofer lines. X-ray spectroscopy was utilized by Moseley (1912) to determine the precise location of elements in the Periodic system. Since then, a number of sophisticated and highly specialized techniques have been developed including Raman spectroscopy, nuclear magnetic resonance, nuclear quadrupole resonance, dynamic reflectance spectroscopy, microwave and gamma ray spectroscopy, and electron paramagnetic resonance.

**Spectrum.** The radiant energy emitted by a substance as a characteristic band of wavelengths, by which it can be identified.

**Spectrum Line.** See spectral line.

**Spin Echo Technique.** A variation of the nuclear magnetic resonance technique in which the radio frequency field is applied in two pulses, separated by a time interval  $t$ , and a strong nuclear induction signal is observed at a time  $t$  after the second pulse.

**Spinning Band Column.** An analytical distillation column inside of which is a series of driven, spinning bands; centrifugal action of the bands throws a layer of liquid onto the inner surface of the column; used as an aid in liquid-vapor contact.

**Spiral Plate Exchanger.** A heat-transfer device made from a pair of plates rolled in a spiral to provide two relatively long, rectangular passages for heat-transfer between fluids in countercurrent flow.

**Spot Test.** The addition of a drop of reagent to a drop or two of sample solution to obtain distinctive colors or precipitates; used in qualitative analysis.

**Spray Tower.** A vertical column, at the top of which is a liquid spray device; used to contact liquids with gas streams for absorption, humidification, or drying.

**Stability Constant.** Refers to the equilibrium reaction of a metal cation and a ligand to form a chelating mononuclear complex; the absolute-stability constant is expressed by the product of the concentration of products divided by the product of the concentrations of the reactants; the apparent-stability constant (also known as the conditional-or effective-stability constant) allows for the nonideality of the system because of the combination of the ligand with other complexing agents present in the solution.

**Standard Calomel Electrode.** A mercury-mercurous chloride electrode used as a reference (standard) measurement in polarographic determinations.

**Standard Deviation :** The standard deviation  $\sigma$  for an infinite no. of measurements is given by,

$$\sigma = \sqrt{\frac{\sum (x_i - \mu)^2}{N}}$$

Where  $\mu$  is the arithmetic mean and  $x_i$  is the particular experimental value and  $N$  is the no. of observations made in experiment. If the no. of observation is finite, then standard

deviation  $\mu$  is represented by  $S$  which is equal :

$$S = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2}$$

**Standard Electrode Potential.** The reversible or equilibrium potential of an electrode in an environment where reactants and products are at unit activity.

**Standard Potential.** The potential of an electrode composed of a substance in its standard state, in equilibrium with ions in their standard states compared to a hydrogen electrode.

**Starch.** Any one of a group of carbohydrates or polysaccharides, of the general composition  $(C_6H_{10}O_5)_n$ , occurring as organized or structural granules of varying size and markings in many plant cells; it hydrolyzes to several forms of dextrin and glucose; its chemical structure is not completely known, but the granules consist of concentric shells containing at least two fractions: an inner portion called amylose, and an outer portion called amylopectin.

**Stark Effect.** The effect on spectrum lines of an electric field which is either externally applied or is an internal field caused by the presence of neighbouring ions or atoms in a gas, liquid, or solid. Also known as electric field effect.

**Steam Distillation.** Distillation carried out in a current of steam with the object of distilling out or particular component of a mixture, or of avoiding too high a temperature during distillation. As normally carried out, the operation consists of distilling a mixture of two immiscible liquids (e.g. chlorobenzene and water) in a current of steam. The ratio of the weights of the two substances distilling is  $(m_1 p_1 / m_2 p_2)$ , where  $m_1$  and  $m_2$  are the molecular weights of the two substances and  $p_1$  and  $p_2$  are their respective vapour pressures at the distillation temperature. Substances with a relatively high molecular weight may be steam distilled over in relatively large amounts in spite of the fact that they may have relatively low vapour pressures at the temperature of distillation.

**Steam Still.** A still in which steam provides most of the heat; distillation requires a lower temperature than in standard equipment (except for a vacuum distillation unit).

**Stern-Gerlach Effect.** The splitting of a beam of atoms passing through a strong, inhomogeneous magnetic field into several beams.

**Still.** Any apparatus or plant in which distillation is carried out.

**Stoichiometry.** The numerical relationship of elements and compounds as reactants and products in chemical reactions.

**Stokes' Law.** The wavelength of luminescence excited by radiation is always greater than that of the exciting radiation.

**Stroke Line.** A spectrum line in luminescent radiation whose wavelength is greater than that of the radiation which excited the luminescence, and thus obey Stokes' law.

**Stop Point.** A term use in laboratory distillation tests. The percentage distillate obtained at a stop point is that amount obtained when the source heat has been removed from the flask at the specified temperature and the apparatus allowed to drain for two minufes.

**Stp.** Standard temperature and pressure.

**Stripping.** The separation of the more volatile component(s) of a liquid mixture from the less volatile component (s) in such a way that the latter is obtained in a pure state, but the former not necessarily so. Stripping may be carried out either by a process of fractional distillation or by bringing the mixture into contact with an inert gas into which the light material with diffuse and be carried away. A stripping column or stripper is used in either case. This is similar to a rectifying columun except that the feed is introduced at the top, instead of part way up, and no reflux is employed. Is an inert gas is being used it is introduced at the bottom of the column and no reboiler is necessary.

Stripping is used for such purposes as the removal of benzole from the oil used to absorb it from coal gas and the removal of light ends from petroleum fractions. In both cases stream is used as the stripping agent.

**Stripping Analysis.** An analytic process of solutions or concentrations containing ions, in which the ions are electrodeposited onto an electrode, stripped (dissolved) from the material from the electrode, and weighed.

**Stripping Reaction.** A nuclear reaction in which part of the incident nucleus combines with the target nucleus, and the other part proceeds with most of its original momentum in practically its original direction; especially the reaction in which the incident nucleus is a deuteron and only a proton emerges from the target.

**Structural Formula.** A system of notation used for organic compounds in which the exact structure, if it is known, is given in schematic representation.

**Structural Group Analysis.** Analytical methods used to obtain a hypothetical, statistical average molecule of a complex mixture of hydrocarbons. The information obtained is usually reported in terms of the carbon skeleton, *e.g.* %  $C_P$  being the % carbon in paraffinic chains, also %  $C_A$  and %  $C_N$  for carbon in aromatic and naphthenic rings respectively. Total aromatic and naphthenic rings per average molecule are denoted by  $R_T$ ,  $R_A$  and  $R_N$ .

The direct method of analysis involves determination of molecular weight and elemental analysis before and after hydrogenation. A rapid, much-used method is the n-d-M method, based on the correlation of physical measurements with the direct method.

**Sublimatography.** A procedure of fractional sublimation in which a solid mixture is separated into bands along a condensing tube with a temperature gradient.

**Submicron.** A term used to describe particles, the size range  $10m\mu$ — $1\mu$ , which are invisible in a ordinary microscope, but sufficiently large to appear in an ultra-microscope.

**Substitution Reaction.** Replacement of an atom or radical by another one in a chemical compound.

**Sulfide.** Any compound with one or more sulfur atom in which the

sulfur is connected directly to a carbon, metal, or other non-oxygen atom; for example, sodium sulfide,  $\text{Na}_2\text{S}$ .

**Sulphonation.** The formation of a sulfonic acid *i.e.*, a compound containing the  $-\text{SO}_2\text{OH}$  group. The conversion of benzene ( $\text{C}_6\text{H}_6$ ) into benzenesulfonic acid ( $\text{C}_6\text{H}_5\text{SO}_2\text{OH}$ ) is an example. Common sulfonating agent are : concentrated sulfuric acid, fuming sulfuric acid, sulfur trioxide, alkali disulfates, pyrosulfates, chlorosulfonic acid and a mixture of manganese dioxide and sulfurous acid.

**Superconductivity.** The phenomenon that causes certain metals, alloys, and compounds near absolute zero to lose both electrical resistance and magnetic permeability, *i.e.*, to have infinite electrical conductivity. Depending upon the substance, the maximum temperature (transition temperature) for the behaviour is  $0.5\text{--}18^\circ\text{K}$ . Superconductivity does not occur in alkali metals, noble metals, ferro and antiferro-magnetic metals. It is well-known in elements having 3, 5, or 7 valence electrons per atom, and is associated with high room-temperature resistivity. A system for transmitting electric current underground by means of superconducting cables has been developed.

**Swarts Reaction.** The reaction of chlorinated hydrocarbons with metallic fluorides to form chlorofluorohydrocarbons, such as  $\text{CCl}_2\text{F}_2$ , which is quite inert and nontoxic.

**Symmetric Top Molecule.** A nonlinear molecule which has one and only one axis of threefold or higher symmetry.

## T

**Tanabe—Sugano Diagram.** Graphs showing the relation between the splitting of electronic energy levels ( $E/B$ ) and crystal

field stabilization energy ( $E/B$ ) where  $B$  is a Racah parameter. Used in assigning electronic transitions in complexes and obtaining values of  $E$  and  $B$ .

**Tartar Emetic**  $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ . A transparent crystalline compound, soluble in water; used to attract and kill moths, wasps, and yellow jackets. Also known as antimony potassium tartrate; potassium antimonyl tartrate.

**Tauber Test.** A color test for identification of pentose sugars; the sugars produce a cherry-red color when heated with a solution of benzidine in glacial acetic acid.

**TEMA Standard.** Shell-and-tube heat-exchange standard designed to supplement the ASME code for unfired pressure vessels.

**Temporary Hardness.** The portion of the total hardness of water that can be removed by boiling whereby the soluble calcium and magnesium bicarbonate are precipitated as insoluble carbonates.

**Term.** A set of  $(2S+1)(2L+1)$  atomic states belonging to a definite configuration and to definite spin and orbital angular momentum quantum numbers  $S$  and  $L$ .

**Ternary System.** Any system with three nonreactive components; in liquid systems, the components may or may not be partially soluble.

**Testing, Chemical.** Identification of a substance by means of reagents, chromatography, spectroscopy, melting and boiling point determination, etc.

**Testing, Physical.** Application of any procedure whose object is to determine the physical properties of a material. There are four major categories of tests: (1) Those that are direct measurements of a property, *e.g.*, tensile strength. (2) Those that subject the material to actual service conditions; these often require a long period of time, *e.g.*, shelf-life of foods and corrosion of metals. (3) Accelerated tests, which require specially designed equipment that simulates service conditions on an exaggerated scale; in these, only a few hours are necessary to duplicate years of service life, *e.g.*, oxygen bomb ageing of elastomers. (4) Nondestructive testing (q.v.) by

x-ray or radiography. Elaborate standard testing procedures are established by the American Society for Testing and Materials (q.v.). The more common types of test are as follows :

abrasion (elastomers, textiles) adhesion (glues, resins)

ageing (elastomers, plastics, leather, food products)

color stability (pigments, organic dyes) (exposure)

corrosion (metals, alloys) (exposure)

dielectric (electrical tapes, plastics, glass)

flammability (textiles, fibres, paper, plastics)

flash point (combustible liquids) (Tag closed cup, Cleveland open cup)

hardness (metals, elastomers, plastics) (Brinell, Rockwell, Shore penetration)

high temperature (elastomers, adhesive)

impact strength (composites, glass, cement)

suncracking (paints, varnishes, elastomers) (exposure)

tear (paper, rubber, textiles)

tensile strength (fibers, elastomers, paper, textiles, metals)

viscosity (lubricants) (Saybolt, Engler)

**Tetradentate Ligand.** A chelating agent which has four groups capable of attachment to a metal ion. Also known as quadridentate ligand.

**Tetrasodium EDTA.** (ethylenediaminetetraacetic acid, tetrasodium salt; EDTA  $\text{Na}_4$ ; sodium edetate).  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{Na}_4\text{O}_8$ , anhydrous or  $2\text{H}_2\text{O}$ . White powder; freely soluble in water. Used as a general-purpose chelating agent.

**Theoretical Plate.** A distillation column plate or tray that produces perfect distillation (that is, produces the same difference in composition as that existing between a liquid mixture and the vapor in equilibrium with it); the packed column equivalent of a theoretical plate is the HETP, or height (of packing equivalent to a theoretical plate).



**Thermal Analysis.** Analytical techniques used for identification and also for investigation of the products of the action of heat on a compound or complex. In differential thermal analysis (DTA) the sample is heated, frequently in an inert atmosphere, and weight is measured as a function of temperature. In differential scanning calorimetry (DSC) electrical heat is added or removed from the samples as the temperature is raised; enthalpy changes due to thermal decomposition are thus followed.

**Thermal Excitation.** The process in which atoms or molecules acquire internal energy in collisions with other particles.

**Thermal-liquid System.** A system with a special liquid that acts as a heat sink or heat source (for example, steam, hot water, mercury, Dowtherm, molten salts, or mineral oils); used for process heating and cooling.

**Thermal Reactor.** A device, system, or vessel in which chemical reactions take place because of heat (no catalysis); for example, thermal cracking, thermal reforming, or thermal polymerization.

**Thermal Titration.** See thermometric titration.

**Thermoanalysis.** See thermal analysis.

**Thermobalance.** At analytical balance modified for thermogravimetric analysis, involving the measurement of weight changes associated with the transformations of matter when heated.

**Thermogravimetric Analysis (TGA).** It is a technique in which the mass of a sample is recorded continuously as its temperature is increased linearly from ambient to as high as 1200°C. A plot of mass as a function of temperature is called thermogram, and it provides both qualitative and quantitative information about the process of heating on a sample.

The apparatus required for the thermogravimetric analysis contains :

- (1) a precision balance,
- (2) a furnace which can go upto a temperature of 1200° to 1500°C.

- (3) Temperature controller and programmer.
- (4) A recording device which plots sample mass as a function of temperature.
- (1) Precision Balance : The Cahn electromagnetic balance is used in several thermogravimetric systems. The sample holder of this balance is supported from a lever arm attached to a galvanometer coil. Deflection of the beam from its rest position by a change in mass is determined photoelectrically. The resulting photo current is then amplified and fed into the galvanometer coil in such a direction as to restore the beam to its original position. The amplified current also determines the position of a recorder pen.

In a Mettler thermobalance, the sample holder is placed in a furnace that is thermally isolated from the remainder of the balance. A change in sample mass causes a deflection of the beam, which interposes a light shutter between a lamp and one of the two photodiodes. The resulting imbalance in the photodiode current is amplified and fed into a coil which is placed between the pole pieces of a permanent magnet. The magnetic field generated by the current in the coil restores the beam to its original position. The amplified photodiode current also determines the position of the pen of a recorder. The Mettler instrument has several weight ranges (1, 10, 100, and 1000 mg) and has a reproducibility of  $\pm 10 \mu\text{g}$ .

- (2) Furnace : The furnace of a thermogravimetric apparatus is generally programmed to increase the temperature linearly at predetermined rates ( $0.5^\circ$  to  $25^\circ\text{C}$  per minute). Temperature range for most instruments is of the order of  $1200^\circ\text{C}$ . Temperatures are determined by a thermocouple located as close as possible to the sample. Insulation and cooling of the exterior of the furnace is required to avoid the heat transfer to the balance. Nichrome winding gives  $1100^\circ\text{C}$ . Pt-Rh gives  $1450^\circ\text{C}$ . Higher temperatures can be obtained by graphite tube furnace.

- (3) **Temperature Controller and Programmer :** A desired rate of heating can be achieved by programming the controller such that the rate of heating is controlled and hence the temperature increases steadily and linearly at different time intervals.
- (4) **A recorder :** The recorder is a photographic device in which the position of the light beam falling on the photographic paper is recorded at different temperatures, such that on washing the photographic paper the positions can be clearly indicated. Simultaneous recording of DTA, TG, and DTG is possible in the same photographic paper by proper selection and control of galvanometers for each technique.

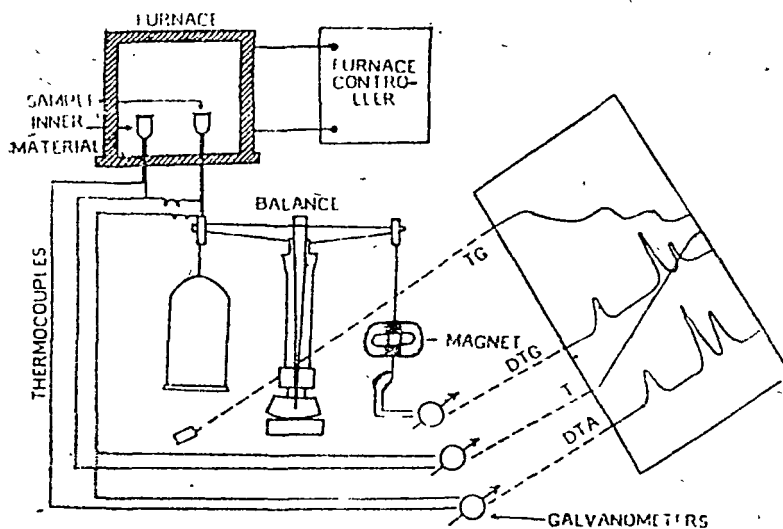
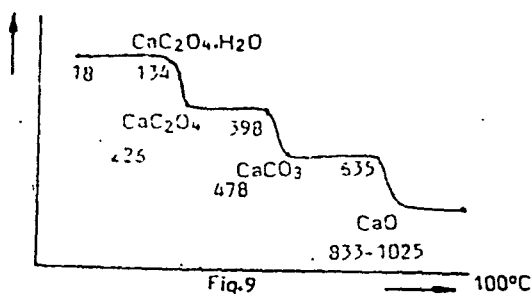


Fig. 8.

The applications of Thermogravimetry as an analytical technique are as follows :

- (1) **Plateaus** on the decomposition curve, indicate constant weight replacement, stable phases over the particular temperature interval. An inflection may imply the formation of an intermediate compound, or the adsorption of volatile product on (or in) the new solid phase.

- (2) In figure 9, thermogram of  $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$  is given. This figure indicates one of the important applications of thermogravimetry, namely that of defining that thermal conditions are necessary to produce a pure weighing form for the gravimetric determination of a sample.



- (3) Fig. 10 indicates the application of thermogravimetry to the quantitative analysis of a mixture of Calcium, Strontium and Barium oxalates. The three ions are first precipitated as the monohydrated oxalates. The mass in the temperature range between  $250^{\circ}$  and  $260^{\circ}\text{C}$  is that of the three anhydrous compounds,  $\text{CaC}_2\text{O}_4$ ,  $\text{SrC}_2\text{O}_4$ , and  $\text{BaC}_2\text{O}_4$  while the mass between  $560^{\circ}$ - $620^{\circ}\text{C}$  corresponds to the weights of three carbonates. The weight change in the next two steps results from the loss of  $\text{CO}_2$ , as first  $\text{CaO}$  and then as  $\text{SrO}$ . Clearly sufficient data are available in the thermogram to calculate the weight of each of the three elements present in the sample.

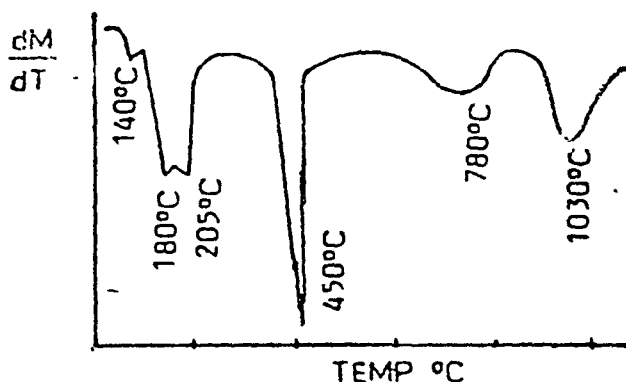


Fig. 10 Differential Thermogram

Fig. 11 is the derivative of thermogram shown in Fig. 10. Many modern instruments are provided with electronic circuitry to provide such a curve as well as the thermogram itself. The derivative curve may give information that is not detectable in the ordinary thermogram. For example the three peaks at  $140^{\circ}$ ,  $180^{\circ}$ ,  $205^{\circ}$  suggest that the three hydrates lose moisture at different temperatures. However all appear to lose carbon monoxide simultaneously and thus yield a single sharp peak at  $450^{\circ}\text{C}$ .

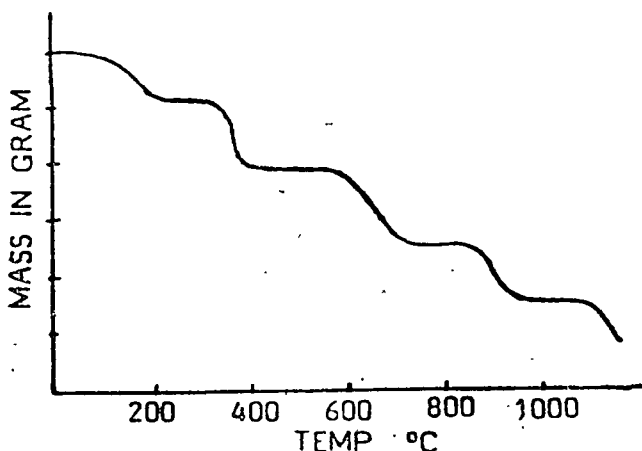


Fig. 11 Thermogram

- (4) By measurements of thermogravimetry we can determine the oxide, hydroxide and carbonate of calcium present in cement or free lime in calcium silicate.
- (5) Thermal stability of chelates, clays, minerals, oxalates metal amine complexes can be established by thermogravimetry.
- (6) Drying of  $\text{Na}_2\text{CO}_3$  is important in acidimetry. The drying temperature can be obtained by thermogravimetry.
- (7) The most important application of thermogravimetric methods are found in the study of polymers. Thermograms provide decomposition mechanisms for various polymeric preparations. In addition the decomposition patterns are characteristic for each kind of polymer and hence can be used for identification purposes.

- (8) Thermogravimetric data can be used to evaluate kinetic parameters of weight changes in reactions. Graphical methods for the determination of order of reaction  $\times$  and the activation energy EA can be obtained from the equation.

$$\frac{-E}{\Delta \log W_r} \frac{A/2.303 R \Delta T^{-1}}{\Delta \log W_r} = -X + \frac{\log (dw/dr)}{\Delta \log W_r}$$

Where R = gas constant

T = absolute temp.

$W_r = (W_0 - W)$

W = Weight loss at completion of reaction.

$W^C$  = Weight loss at time t.

The shape of a thermogram for a particular compound is influenced by :

- (a) heating rate,
  - (b) the sample,
  - (c) the crucible and
  - (d) the atmosphere.
- (a) Heating rate : At a given temperature, the extent of decomposition is greater for slow rate of heating than at faster rate. The rate of reaction of the sample will affect the difference between the sample temperature and furnace temperature depending on whether the reaction is exothermic or endothermic.
  - (b) Sample : Use of small finely divided sample is preferred.
  - (c) Atmosphere : The environmental atmosphere immediately surrounding the reacting particles influences the curve. Even small changes in the composition of this atmosphere can affect the thermogram.

**Thermogravimetric Analysis.** Chemical analysis by the measurement of weight changes of a system or compound as a function of increasing temperature.

**Thermogravitational Column.** A device in which thermal diffusion results from the countercurrent flow of hot and cold material,

thus increasing the separation of materials in a solution by the formation of a concentration gradient (difference). Also known as Clausius-Dickel column.

**Thermokinetic Analysis.** A type of enthalpimetric analysis which uses kinetic titrimetry; involves rapid and continuous automatic delivery of a suitable titrant, under judiciously controlled experimental conditions with temperature measurement; the end points obtained are converted by mathematical procedures into valid stoichiometric equivalence points and used for determining reaction rate constants.

### **Thermoluminescence**

1. Broadly, any luminescence appearing in a material due to application to heat.
2. Specifically, the luminescence appearing as the temperature of a material is steadily increased; it is usually caused by a process in which electrons receiving increasing amounts of thermal energy escape from a centre in a solid where they have been trapped and go over to a luminescent center, giving it energy and causing it to luminesce.

**Thermometric Analysis.** A method for determination of the transformations a substance undergoes while being heated or cooled at an essentially constant rate, for example, freezing-point determinations.

**Thermometric Titration.** A titration in an adiabatic system, yielding a plot of temperature versus volume of titrant; used for neutralization, precipitation, redox, organic condensation, and complex-formation reactions. Also known as calorimetric titration; enthalpy titration; thermal titration.

**Thermosiphon Reboiler.** A liquid reheater (as for distillation-column bottoms) in which natural circulation of the boiling liquid is obtained by maintaining a sufficient liquid head.

**Thin-layer Chromatography (TLC).** A micro type of chromatography (q.v.). The thin layer (about 0.01 inch) is the adsorbent, usually a special silica gel spread on glass, or incorporated in a plastic film. Single drops of the solutions to be investi-

gated are placed along one edge of the glass plate, and this edge then dipped into a solvent. The solvent carries the constituents of the original test drops up the thin layer in a selective separation, so that a comparison with known standards, and various identifying tests may be made on the spots formed.

**Thin-layer Chromatography.** Chromatographing on thin layers of adsorbents rather than in column; adsorbent can be alumina, silica gel, silicates, charcoals, or cellulose.

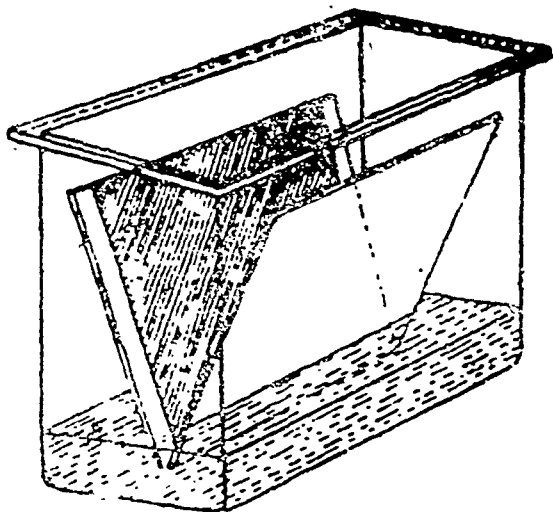


Fig. 5

In thin layer chromatography a thin layer of adsorbent is coated on a glass plate which acts as a stationary phase. A solvent is used as a mobile phase which dissolves the solute to a different extent from a mixture of solution placed on the stationary phase. From the  $R_f$  values of different components, separation can be achieved.

Due to its simplicity, high resolution, easy recovery of separated components, TLC has been found to be widely used in industry. In this technique, a suitable adsorbent like silica gel is finely ground and made into a slurry in water and spread over a glass plate with a spreader and thin film of adsorbent (0.15–0.2 mm thickness) to thus made on a glass

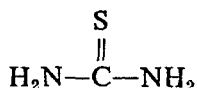


plate. The plate is then activated at  $100^\circ\text{C}$  in an oven. A very small quantity of solution dissolved in water is then applied to the plate by a micropipette. The spot line of sample is marked and the plate is now placed in a solvent tank vertically such that solvent moves through the plate due to capillary action, dissolving different solutes to a different extent due to their different  $R_f$  value. Colourless solutes can be located under an ultra violet lamp. From the  $R_f$  values of components, identification of different substances is possible.

**Thionyl Chloride  $\text{SOCl}_2$ .** A toxic, yellowish to red liquid with a pungent aroma, soluble in benzene, decomposes in water and at  $140^\circ\text{C}$ ; boils at  $79^\circ\text{C}$ ; used as a chemical intermediate and catalyst. Also known as sulfur oxychloride; sulfurous oxychloride.

**Thiosemicarbazide  $\text{NH}_2\text{CSNHNH}_2$ .** A white, water and alcohol-soluble powder melting at  $182^\circ\text{C}$ ; used as an analytical reagent and in photography and rodenticides. Also known as amino-thiourea.

### Thiourea



Bismuth salts give a yellow solution with the reagent in acid solution. The interference is due to  $\text{Sb}^{3+}$ ,  $\text{Hg}_2^{2+}$ , and  $\text{Ag}^+$ .

Test Place 1 drop of the test solution on a spot plate and add 1 drop of a 10 per cent aqueous solution of reagent and one drop of dil.  $\text{HNO}_3$ .

A yellow solution indicates bismuth, the limit of identification being  $2.5 \mu\text{g Bi}$ ; conc. limit, 1 in 30,000.

**Thunburg Technique.** A technique used to study oxidation of a substrate occurring by dehydrogenation reactions; methylene blue, a reversibly oxidizable indicator, substitutes for molecular oxygen as the ultimate hydrogen acceptor (oxidant), becoming reduced to the colorless leuco form.

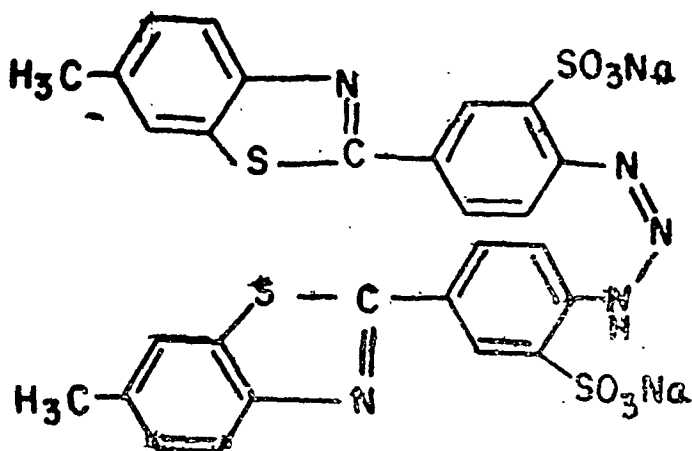
**Thylox Process.** The conversion of coke oven-gas, hydrogen sulfide, into elemental sulfur by absorption in a solution of arsenious

oxide and soda ash in water, then air-blowing to liberate the sulfur which can be skimmed off the solution.

**Time-off-flight Mass Spectrometer.** A mass spectrometer in which all the positive ions of the material being analyzed are ejected into the drift region of the spectrometer tube with essentially the same energies, and spread out in accordance with their masses as they reach the cathode of a magnetic electron multiplier at the other end of the tube.

**Time-resolved Laser Spectroscopy.** A method of studying transient phenomena in the interaction of light with matter through the exposure of samples to extremely short and intense pulses of laser light, down to subnanosecond or subpicosecond duration.

**Titan Yellow Reagent.** Magnesium salts form bright red ppt. in



causic alkaline solution in the presence of  $\text{CN}^-$ . The interference is due to Cu and Mn. But these ions can be removed by precipitating as sulphides with  $\text{Na}_2\text{S}$ .

Test Place 1 drop of the test solution on a spot plate. Add 2 drops of 5N KCN solution and 1 drop of 4N NaOH solution. Stir the solution thoroughly and now add 1 drop of the reagent solution (0.1% aqueous solution).

A bright red ppt. or colour indicates magnesium, the limit of identification being 1.5  $\mu\text{g}$ ; Mg; conc. limit, 1 in 33,000.

**Titer.** In solutions :

- (1) the concentration of a dissolved substance as determined by titration;
- (2) the minimum amount or volume needed to bring about a given result in titration; or
- (3) the solidification point of fatty acids which have been liberated from the fat by hydrolysis.

**Titrand.** The substance that is analyzed in a titration procedure.

**Titrant.** A standard solution of known concentration and composition used for analytical titrations.

**Titration.** A process for determining the volume of one solution required to react quantitatively with a given volume of another in which one solution is added to the other, a small amount at a time until just sufficient has been added to complete the reaction (equivalence point). The equivalence point is determined as an end-point by, *e.g.*, cessation of precipitation ( $\text{Ag}^+$  plus  $\text{Cl}^-$ ), colour change (oxalate plus  $\text{MnO}_4^-$ ) use of an indicator, or by use of electrical methods (electrometric, conductimetric, titrations). Titrations may be carried out by hand from a burette or automatically.

**Tollen's Aldehyde Test.** A test that uses an ammoniacal solution of silver oxides to test for aldehydes and ketones.

**Tollens Reagent.** An ammoniacal solution of silver oxide which is used as a test for aldehydes, which, unlike ketones, cause the deposition of a silver mirror.

**Top Steam.** Steam admitted near the top of a shell still to purge the still, and to prevent a vacuum from forming when pumping out the liquid contents.

**Total Heat of Dilution.** See heat of dilution.

**Total Heat of Solution.** See heat of solution.

**Tower.** A vertical, cylindrical vessel used in chemical and petroleum processing to increase the degree of separation of liquid mixtures by distillation or extraction. Also known as column.

**Trace Analysis.** Analysis of a very small quantity of material of a sample by such techniques as polarography or spectroscopy.

**Trace Element.** A nonessential element found in small quantities (usually less than 1.0%) in a mineral. Also known as accessory element; guest element.

**Tracer.** A foreign substance; usually radioactive, that is mixed with or attached to a given substance so the distribution or location of the latter can later be determined; used to trace chemical behavior of a natural element in an organism. Also known as tracer element.

**Transfer Unit.** The relationship between the overall rate coefficient (for whatever transfer operation is being calculated), column volume, and fluid volumetric flow rate in fixed-bed sorption operations.

**Transmission Diffraction.** A type of electron diffraction analysis in which the electron beam is transmitted through a thin film or powder whose smallest dimension is no greater than a few tenths of a micrometer.

**Transmittance.** During absorption spectroscopy, the amount of radiant energy transmitted by the solution under analysis.

**Transport Number.** The fraction of the total current carried by a given ion in an electrolyte.

**Traveling-screen Dryer.** A moving screen belt on which damp material is conveyed through a heated drying zone. Also known as screen dryer.

**Tray Tower.** A vertical process tower for liquid-vapor contacting (as in distillation, absorption, stripping, evaporation, spray drying, dehumidification, humidification, flashing, rectification, dephlegmation), along the height of which is a series of trays designed to cause intimate contact between the falling liquid and the rising vapor.

**Treater.** A vessel or system for the contacting of a process stream with reagent (treating) chemicals; for example, acid treating or caustic treating.

**Triple Point.** A particular temperature and pressure at which three different phases of one substance can coexist in equilibrium.

**Triplet State.** Electronic state of an atom or molecule whose total spin angular momentum quantum number is equal to 1.

**Trouton's Rule.** An approximation rule for the derivation of molar heats of vaporization of normal liquids at their boiling points.

**True-boiling-point Analysis.** A standard laboratory technique used to predict the refining qualities of crude petroleum; gives distillation cuts for gasoline, kerosine, distillate (diesel) fuel, cracking, and lube distillate stocks. Also known as true-boiling-point distillation.

**True Freezing Point.** The temperature at which the liquid and solid forms of a substance exist in equilibrium at a given pressure (usually 1 standard atmosphere, or 101,325 newtons per square meter).

**Turbidimetric Analysis.** A scattered-light procedure for the determination of the weight concentration of particles in cloudy, dull, or muddy, solutions; uses a device that measures the loss in intensity of a light beam as it passes through the solution. Also known as turbidimetry.

**Turbidimetric Titration.** Titration in which the end point is indicated by the developing turbidity of the titrated solution.

**Turbidimetry.** A method of quantitative analysis which involves the spectrophotometric estimation of absorption by a colloidal dispersion of a precipitate.

### **Turbidity**

1. Measure of the clarity (using APHA or colorimetric scales) of an otherwise clear liquid.
2. Cloudy or hazy appearance in a naturally clear liquid caused by a suspension of colloidal liquid droplets or fine solids.

**Turbidity Indicators.** The use of *e.g.* a weak organic acid which flocculates in the presence of a slight excess of hydrogen ions as an indicator for pH titrations. The applications are

- restricted but are used in titrations of e.g. glycine where the change in pH near the equivalence-point is slow.

**Turbidity Point.** The point in a titration at which a turbidity indicator shows flocculation.

**Turbogrid Plate.** A tray for distillation columns that consists of a flat grid of parallel slots extending over the entire cross-sectional area of the column; the liquid level on each tray is maintained by a dynamic balance between down-flowing liquid and up-flowing vapor.

**Turnaround.** In petroleum refining, the shutdown of a unit after a normal run for maintenance and repair work, then putting the unit back into operation.

**Turnbull's Blue.** A blue pigment that precipitates from the reaction of potassium ferricyanide with a ferrous salt.

### **Turnover Number**

1. The number of molecules of a substrate acted upon in a period of 1 minute by a single enzyme molecule, with the enzyme working at a maximum rate.
2. In an industrial catalytic process, a value that indicates the amount of feed or substrate converted per a measured amount of catalyst.

**Twin Law.** A statement relating two or more individuals of a twin to one another in terms of their crystallography (twin, plane, twin axis, and so on).

**Twinning.** The development of a twin crystal by growth, translation, or gliding.

**Twinning Plane.** See twin plane.

**Tow-dimensional Chromatography.** A paper chromatography technique in which the sample is resolved by standard procedures (ascending, descending, or horizontal solvent movement) and then turned at right angles in a second solvent and re-resolved.

# U

**Ultimate Analysis.** A determination of the % of every element in a compound without regard to its molecular structure.

**Ultrafiltration.** Separation of colloidal or very fine solid materials by filtration through microporous or semipermeable mediums.

**Ultrafining.** A proprietary fixed-bed catalytic hydrogenation process used in petroleum refineries to desulfurize and upgrade naphtha distillates.

**Ultraforming.** A proprietary catalytic reforming process used to increase the octane ratings of petroleum naphthas.

**Ultraviolet.** Radiation in the region of the electromagnetic spectrum including wavelengths from 100 to 3900 Å.

**Hazard :** Dangerous to eyes; overexposure may cause severe skin burns (sunburn).

**Uses :** Air sterilization in hospitals; microscopy.

**Ultra-violet Absorbers, Light Stabilizers.** Compounds which absorb u.v. light and dissipate energy harmlessly. Used to protect polymers against photolytic degradation and also in sun-tan lotions. Most light stabilizers are aromatic compounds with the aromatic ring conjugated with a C=O or N system.

**Ultraviolet Absorption Spectrophotometry.** The study of the spectra produced by the absorption of ultraviolet radiant energy during the transformation of an electron from the ground state to an excited state as a function of the wavelength causing the transformation.

**Ultraviolet Densitometry.** An ultraviolet-spectrophotometry technique for measurement of the colors on thin-layer chromatography absorbents following elution.

**Ultraviolet Photoemission Spectroscopy.** A spectroscopic technique in which photons in the energy range 10-200 electronvolts bombard a surface and the energy spectrum of the emitted electrons gives information about the states of electrons in atoms and chemical bonding. Abbreviated UPS.

**Ultraviolet Spectrometer.** A device which produces a spectrum of ultraviolet light and is provided with a calibrated scale for measurement of wavelength.

**Ultraviolet Spectrophotometry.** Determination of the spectra of ultraviolet absorption by specific molecules in gases or liquids (for example,  $\text{Cl}_2$ ,  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{CS}_2$ , ozone, mercury vapor, and various unsaturated compounds).

**Ultraviolet Spectroscopy.** Absorption spectroscopy involving electromagnetic wavelengths in the range 4-400 nanometers.

**Ultraviolet Stabilizer.** See UV stabilizer.

**Undercutting.** In distillation, the technique of taking the products coming off the distillation tower at a temperature below the desired ultimate boiling point range to prevent contaminating the products with the compound that would distill just beyond the ultimate boiling point range.

**Underwood Chart.** A graphical solution of mass balances for a single equilibrium stage in the calculation of a solvent-extraction operation.

**Underwood Distillation Method.** A method for calculation of liquid separations from binary distillation systems operated at partial reflux.

**Unfired Pressure Vessel.** A pressure vessel that is not in direct contact with a heating flame.

**Unisol Process.** A proprietary solvent extraction process used in petroleum refineries to extract mercaptan sulfur and certain nitrogen compounds from sour gasolines or distillates.

**Unit Operations.** The basic physical operations of chemical engineering in a chemical process plant, that is distillation, fluid



transport, heat and mass transfer, evaporation, extraction, drying, crystallization, filtration, mixing, size separation, crushing and grinding, and conveying.

**Upflow.** In an ion-exchange unit, an operation in which solutions enter at the bottom of the unit and leave at the top.

**Upstream.** That portion of a process stream that has not yet entered the system or unit under consideration; for example, upstream to a refinery or to a distillation column.

**Orange Zinc Acetate Reagent.** Sodium salts form yellow colour or ppt. with the reagent.

*Test.* Take 2 drops of the test solution on a black watch glass and add 8 drops of the reagent solution. Stir the solution with the glass rod.

A yellow colour or ppt. indicates sodium, the limit of identification being 12.5 big sodium; conc. limit, 1 in 400.

**USP Acid Test.** A United States Pharmacopoeia test to determine the carbonizable substances present in petroleum white oils.

**U.V. Spectroscopy.** For U. V. Spectra, the source must be producing energy in the U.V. region which can be absorbed by molecules and the absorption is recorded by a suitable device. The continuous U.V. source is produced by electrical excitation of hydrogen of Deuterium at low pressures.

*Prism Monochromator:* For visible regions, prisms and lenses of glass are used and U.V. region quartz prisms and lenses are used as glass absorbs in the U.V. region.

1. *Reflection gratings:* They are made by ruling a large number of equidistant lines on a polished metal surface like Aluminium. As many as 15000 to 30,000 lines per inch will be made on the metal surface.
2. *Transmission gratings* are produced by drawing lines on a glass surface.

The applications of U. V. and visible spectrophotometry are as follows :

1. Titrations in which absorbance of a solution is used to determine the end point are called photometric titrations. The method is based on the fact that the absorbance of a solution is directly proportional to the concentration. During the course of titration, the concentration of solution being titrated changes, and the absorbance of the solution will also change.
2. From the absorption spectra in the ultraviolet regions qualitative information about the functional groups such as carbonyl, nitro, amino, etc, can be obtained. This information is used to identify organic compounds.
3. From absorption spectra, quantitative analysis of samples of the concentration of  $10^{-6}$  M can be determined. Absorption at different wavelengths can be studied to identify different components in a mixture. It is widely used in air and water pollution studies.
4. In the study of complexes, and the determination of dissociation constants of acids and bases.

## V

**Vacuum Condensing Point.** Temperature at which the sublimate (vaporized solid) condenses in a vacuum. Abbreviated vcp.

**Vacuum Crystallizer.** Crystallizer in which a warm saturated solution is fed to a lagged, closed vessel maintained under vacuum; the solution evaporates and cools adiabatically, resulting in crystallization.

**Vacuum Distillation.** Distillation at a pressure less than atmospheric but not so low that it would be classed as molecular distillation. Since lowering the pressure also lowers the boiling point,

vacuum distillation is useful for distilling high-boiling and heat-sensitive materials such as heavy distillates in petroleum, fatty acids, vitamins, etc.

**Vacuum Flashing.** The heating of a liquid that, upon release to a lower pressure (vacuum), undergoes considerable vaporization (flashing). Also known as flash vaporization.

**Vacuum Thermobalance.** An instrument used in thermogravimetry consisting of a precision balance and furnace that have been adapted for continuously measuring or recording changes in weight of a substance as a function of temperature; used in many types of physicochemical reactions where rates of reaction and energies of activation for vaporization, sublimation, and chemical reaction can be obtained.

**Vacuum Pump.** A pump designed to extract gas from a space where the pressure is considerably below atmospheric and discharge it to atmosphere. Mechanical pumps used for this purpose are normally of the rotary, positive displacement type and can provide pressures down to about  $1\text{--}3 \text{ N/M}^2$ . In the chemical industry steam jet ejectors are widely used, especially with distillation columns and evaporators, pressures of  $0.13 \text{ bar}$  to  $6.5 \times 10^{-4} \text{ bar}$  being attained, depending on the number of stages. For very high vacua, as in molecular distillation, diffusion pumps are employed.

**Vacuum Ultraviolet Spectroscopy.** Absorption spectroscopy involving electromagnetic wavelengths shorter than  $200 \text{ nanometers}$ ; so called because the interference of the high absorption of most gases necessitates work with evacuated equipment.

**Vaporizer.** A process vessel in which a liquid is heated until it vaporizes; heat can be indirect (steam or heat-transfer fluid) or direct (hot gases or submerged combustion).

**Vapor-liquid Separation.** The removal of liquid droplets from a flowing stream of gas or vapor; accomplished by impingement, cyclonic action, and absorption or adsorption operations.

**Vapor-phase Reactor.** A heavy steel vessel for carrying out chemical reactions on an industrial scale where efficient control over a vapor phase is needed, for example, in an oxidation process.

**Vapor-pressure Osmometer.** A device for the determination of molecular weights by the decrease of vapor pressure or a solvent upon addition of a soluble sample.

**Vapor Rate.** In distillation, the upward flow rate of vapor through a distillation column.

**Variance:** Variance is another quantity used to express precision. It is the square of the standard deviation. It is always a positive quantity.

**Vibrational Energy.** For a diatomic molecule, the difference between the energy of the molecule idealized by setting the rotational energy equal to zero, and that of a further idealized molecule which is obtained by gradually stopping the vibration of the nuclei without placing any new constraint on the motions of electrons.

**Vibrational Level.** An energy level of a diatomic or polyatomic molecule characterized by a particular value of the vibrational energy.

**Vibrational Spectrum.** The molecular spectrum resulting from transitions between vibrational levels of a molecule which behaves like the quantum-mechanical harmonic oscillator.

### **Vibrational Sum Rule**

1. The rule that the sums of the band strengths of all emission bands with the same upper state is proportional to the number of molecules in the upper state, where the band strength is the emission intensity divided by the fourth power of the frequency.
2. The sums of the band strengths of all absorption bands with the same lower state is proportional to the number of molecules in the lower state, where the band strength is the absorption intensity divided by the frequency.

**Victor Meyer Method for Vapour Densities.** Method using the volume occupied by a known weight of vapour (generally measured as expelled air).

**Vigreux Column.** An obsolete apparatus used in laboratory fractional distillation. It is a long glass tube with indentation in its walls; a thermometer is placed at the top of the tube and a side arm is attached to a condenser.

**Viscosity Blending Chart.** A graphical means for estimating the viscosity at a given temperature of a blend of petroleum products.

**Viscosity Breaking.** A petroleum refinery process used to lower or break the viscosity of high-viscosity residuum by thermal cracking of molecules at relatively low temperatures. Also known as visbreaking.

**Viscosity Conversion Table.** A table or chart with which kinematic viscosity, in centistokes, can be converted to Saybolt viscosity, in seconds, at the same temperature.

**Viscosity-gravity Constant.** An index of the chemical composition of crude oil; defined as the general relation between specific gravity and Saybolt Universal viscosity; the constant is low for paraffinic crude oils, high for naphthenic crude oils. Abbreviated VGC.

**Viscosity Index.** An arbitrary scale used to show the magnitude of viscosity changes in lubricating oils with changes in temperature. Abbreviated VI.

**Viscosity-temperature Chart.** A chart with which the kinematic or Saybolt viscosity of a petroleum oil at any temperature within a limited range may be ascertained, provided viscosities at two temperatures are known.

**Visible Absorption Spectrophotometry.** Study of the spectra produced by the absorption of visible-light energy during the transformation of an electron from the ground state to an excited state as a function of the wavelength causing the transformation.

**Visible Spectrophotometry.** In spectrophotometric analysis, the use of a spectrophotometer with a tungsten lamp that has an electromagnetic spectrum of 380—780 nanometers as a light source, glass or quartz prisms or gratings in the monochromator, and a photomultiplier cell as a detector.

### Visible Spectrum

1. The range of wavelengths of visible radiation.
2. A display or graph of the intensity of visible radiation emitted or absorbed by a material as a function of wavelength or some related parameter.

**Visual Colorimetry.** Is the process of identifying the concentration of a coloured substance using human eye as the receptor.

Visual Colorimetry involves :

- (1) the standard series method,
- (2) the duplication method,
- (3) the balancing method.

(1) *Standard series method.* In this method, the intensity of colour of unknown solutions is matched with a series of standard solutions of known concentrations. Initially the colour of the unknown is matched between two standard solutions. To find out the correct concentrations another series of standard solutions are prepared in the range so determined and the intensity is then matched. The method is not very accurate as it may give error in the range  $\pm 3-8\%$ .

(2) *Duplication Method.* In this method, a known volume of the sample solution is placed in a Nessler tube and a measured volume of the reagent is added to get the respective colour. In another Nessler tube an equal volume of water and the same volume of reagent is placed. A standard solution of the species being determined is then placed in the blank using a microburette till the colours of the two solutions match.

- (3) *Balancing Method.* This method is described with reference to the Duboscq colorimeter. The intensity of the colour of the unknown and that of the standard is made in two tubes. The height of the solution in one tube is adjusted in such a way that when the two tubes are viewed vertically downwards, the intensities of the colours of the two are equal. Since the concentration of solution in one tube is known, the other can be calculated using Lambert Beer's law.

**Volhard's Solution.** A solution of potassium thiocyanate used in analytical chemistry.

**Volhard Titration.** Determination of the halogen content of a solution by titration with a standard thiocyanate solution.

**Voltametry.** Any electrochemical technique in which a faradaic current passing through the electrolysis solution is measured while an appropriate potential is applied to the polarizable or indicator electrode; for example, polarography.

**Volume Susceptibility.** The magnetic susceptibility of a specified volume (for example, 1 cubic centimeter) of a magnetically susceptible material.

**Volumetric Analysis.** Quantitative analysis of solutions of known volume but unknown strength by adding reagents of known concentration until a reaction end point (color change or precipitation) is reached; the most common technique is by titration.

**Volumetric Flask.** A laboratory flask primarily intended for the preparation of definite, fixed volumes of solutions, and therefore calibrated for a single volume only.

**Volumetric Pipette.** A graduated glass tubing used to measure quantities of a solution; the tube is open at the top and bottom; and a slight vacuum (suction) at the top pulls liquid into the calibrated section; breaking the vacuum allows liquid to leave the tube.

**Vorce Diaphragm Cell.** A cylindrical cell with graphite anodes and asbestos-covered cathode, used in the electrolytic process for the manufacture of chlorine.

## W

**Wagner's Reagent.** An aqueous solution of iodine and potassium iodide; used for microchemical analysis of alkaloids. Also known as Wagner's solution.

**Wagner's Solution.** See Wagner's reagent.

### Washing

1. In the purification of a laboratory sample, the cleaning of residual liquid impurities from precipitates by adding washing solution to the precipitates, mixing, then decanting, and repeating the operation as often as needed.
2. The removal of soluble components from a mixture of solids by using the effect of differential solubility.
3. In a process operation, cleaning of a solids bed (settler) or cake (filter) with a liquid in which the solid is not soluble.

**Wash Water.** Water contacted with process streams (liquid or gas), packed beds, or filter cakes to flush or dissolve out impurities.

**Waste Heat Boiler.** A boiler which produces steam by utilizing the heat in the gases or liquid from a chemical process, *e.g.* a calcining operation.

**Water Absorption Tube.** A glass tube filled with a solid absorbent (calcium chloride) or silica gel) to remove water from gaseous streams during or after chemical analyses.



**Wavelength Standards.** Accurately measured lengths of waves emitted by specified light sources for the purpose of obtaining the wavelengths in other spectra by interpolating between the standards.

**Wave Number.** The reciprocal of wavelength, *i.e.* the number of waves in a given length (generally 1 cm). Often referred to as frequencies.

**Weaver Flame Speed Factor.** A calculated flame speed factor for flammable gases or vapours based largely on empirical data. The scale used is an arbitrary one with hydrogen given a value of 100.

**Weber Number 3.** A dimensionless number used in interfacial area determination in distillation equipment, equal to the surface tension divided by the product of the liquid density, the acceleration of gravity, and the depth of liquid on the tray under consideration. Symbolized  $N_{we3}$ .

**Wedge Spectrograph.** A spectrograph in which the intensity of the radiation passing through the entrance slit is varied by moving an optical wedge.

**Weiss Magneton.** A unit of magnetic moment, equal to  $1.853 \times 10^{-21}$  erg/oersted, about one-fifth of the Bohr magneton; it is experimentally derived, the magnetic moments of certain molecules being close to integral multiples of this quantity.

**Weisz Ring Oven.** A device for vaporization of solvent from filter paper, leaving the solute in a ring (circular) shape; used for qualitative analysis of very small samples.

**Werner Band.** A band in the ultraviolet spectrum of molecular hydrogen extending from 116 to 125 nanometers.

**Wetted-wall Column.** A vertical column that operates with the inner walls wetted by the liquid being processed; used in theoretical studies of mass transfer rates and in analytical distillations; an example is a spinning-band column.

*Wobbe Index*

**Whirling or Sling Hygrometer.** An instrument for measuring the quantity of water vapour in air consisting of a wet bulb thermometer and a dry bulb thermometer mounted next to each other in a frame, the assembly being whirled around manually.

**Wiedemann's Additivity Law.** The law that the mass (or specific) magnetic susceptibility of a mixture or solution of components is the sum of the proportionate (by weight fraction) susceptibilities of each component in the mixture.

**Wigner-seitz Cell.** A polyhedron about an atom in a face-centered cubic structure, made by drawing planes which perpendicularly-bisect the lines to the nearest neighbors; in a body-centered cubic structure, bisecting planes of lines to nearest neighbors and next-nearest neighbors are used; such polyhedra fill space.

**Wigner Supermultiplet.** A set of quantum-mechanical states of a collection of nucleons which form the basis of a representation of  $SU(4)$ , especially appropriate when spin and isospin dependence of the nuclear interaction may be disregarded; several combinations of spin and isospin multiplets may occur in a supermultiplet.

**Wijs' Iodine Monochloride Solution.** A solution in glacial acetic acid of iodine monochloride; used to determine iodine numbers. Also known as Wijs' special solution.

**Wijs' Special Solution.** See Wijs' iodine monochloride solution.

**Winkler Titration.** A chemical method for estimating the dissolved oxygen in sea-water; manganous hydroxide is added to the sample and reacts with oxygen to produce a manganese compound which in the presence of acid potassium iodide liberates an equivalent quantity of iodine that can be titrated with standard sodium thiosulfate.

**Wobbe Index.** A measure of thermal throughput of a fuel gas in a burner or combustion system. Where the composition of a fuel gas is varied the thermal input to a burner can be kept constant

if the Wobbe index (i.e. calorific value/  $\sqrt{\text{specific gravity}}$ ) is constant. Where the gas pressure is also changed the 'extended Wobbe index' (Wobbe index  $\times \sqrt{\text{pressure}}$ ) must remain constant.

## X

**X-axis.** A reference axis within a quartz crystal.

**X-cut.** A quartz-crystal cut made in such a manner that the x axis is perpendicular to the faces of the resulting slab.

**X-ray Crystallography.** The study of crystal structure by x-ray diffraction techniques. Also known as roentgen diffractometry.

**X-ray Crystal Spectrometer.** An instrument designed to produce an x-ray spectrum and measure the wavelengths of its components, by diffracting x-rays from a crystal with known lattice spacing.

**X-ray Diffraction Analysis.** Analysis of the crystal structure of materials by passing x-rays through them and registering the diffraction (scattering) image of the rays.

**X-ray Emission.** See x-ray fluorescence.

**X-ray Fluorescence.** Emission by a substance of its characteristic x-ray line spectrum upon exposure to x-rays. Also known as x-ray emission.

**X-ray Fluorescence Analysis.** A nondestructive physical method used for chemical analyses of solids and liquids; the specimen is irradiated by an intense x-ray beam and the lines in the spectrum of the resulting x-ray fluorescence are diffracted at various angles by a crystal with known lattice spacing; the elements in the specimen are identified by the wavelengths of their spectral lines, and their concentrations are determined by the intensities of these lines. Also known as x-ray fluorimetry.

**X-ray Fluorescent Emission Spectrometer.** An x-ray crystal spectrometer used to measure wavelengths x-ray fluorescence; in order to concentrate beams of low intensity, it has bent reflecting or transmitting crystals arranged so that the theoretical curvature required can be varied with the diffraction angle of a spectrum line.

**X-ray Fluorimetry.** See x-ray fluorescence analysis.

**X-ray Image Spectrography.** A modification of x-ray fluorescence analysis in which x-rays irradiate a cylindrically bent crystal, and Bragg diffraction of the resulting emissions produces a slightly enlarged image with a resolution of about 50 micrometers.

**X-ray Photoelectron Spectroscopy.** A form of electron spectroscopy in which a sample is irradiated with a beam of monochromatic x-rays and the energies of the resulting photoelectrons are measured. Abbreviated XPS. Also known as electron spectroscopy for chemical analysis (ESCA).

**X-ray Powder Diffractometer.** See powder diffraction camera.

**X-ray Spectrograph.** An x-ray spectrometer equipped with photographic or other recording apparatus; one application is fluorescence analysis.

**X-ray Spectrometer.** An instrument for producing the x-ray spectrum of a material and measuring the wavelengths of the various components.

**X-ray Spectrometry.** The measure of wavelengths of x-rays by observing their diffraction by crystals of known lattice spacing. Also known as roentgen spectrometry; x-ray spectroscopy.

**X-ray Spectroscopy.** See x-ray spectrometry.

**X-ray Spectrum.** A display or graph of the intensity of x-rays, produced when electrons strike a solid object, as a function of wavelengths or some related parameter; it consists of a continuous bremsstrahlung spectrum on which are superimposed groups of sharp lines characteristic of the elements in the target.

**X-ray Unit.** See siegbahn.

**X Unit.** See siegbahn.

## Y

**Yrast State.** An energy state of a nucleus whose energy is less than that of any other state with the same spin.

## Z

**Z Axis.** The optical axis of a quartz crystal, perpendicular to both the x and y axes.

**Zeeman Displacement.** The separation in wave numbers, of adjacent spectral lines in the normal Zeeman effect in a unit magnetic field, equal (in centimeter-gram-second Gaussian units) to  $e/4\pi mc^2$ , where  $e$  and  $m$  are the charge and mass of the electron, or to approximately  $4.67 \times 10^{-15}$  (centimeter) $^{-1}$  (gauss) $^{-1}$ .

**Zeeman Effect.** A splitting of spectral lines in the radiation emitted by atoms or molecules in a static magnetic field.

**Zeeman Energy.** The energy of interaction between an atomic or molecular magnetic moment and an applied magnetic field.

**Zeolite.** A natural hydrated silicate of aluminium and either sodium or calcium or both, of the type  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot x\text{H}_2\text{O}$ ; or an artificial ion-exchange resin. Both natural and artificial zeolites

### *Zero-order Reaction*

are used extensively for water softening and as detergent builders. For the former purpose the sodium or potassium compounds are required, since their usefulness depends on the cationic exchange of the sodium of the zeolite for the calcium or magnesium of hard water. When the zeolite has become saturated with calcium or magnesium ion, it is flooded with strong salt solution; a reverse exchange of cations takes place, and the material is regenerated. The natural zeolites are analcite, chabazite, heulandite, natrolite, stilbite, and thomsonite.

Artificial zeolites are made in a variety of forms ranging from gelatinous to porous and sandlike, and are used as gas adsorbents, drying agents, and catalysts as well as water softeners. They include such diverse groups of compounds of sulfonated organics or basic resins, which act in a similar manner to effect either cation or anion exchange.

**Zeotrope.** A nonazeotropic liquid mixture which may be separated by distillation, and in which the components are miscible in all proportions (homogeneous zeotrope or homozeotrope) or not miscible in all proportions (heterogeneous zeotrope or heterozeotrope).

**rewitinoff Reagent.** A light-colored methylmagnesium iodide-n-butyl ether solution that reacts rapidly with moisture and oxygen; used to determine water, alcohols, and amines in inert solvents.

**Zero Branch.** A spectral band whose Fortrat parabola lies between two other Fortrat parabolas, with its vertex almost on the wave number axis.

**Zero-order Reaction.** A reaction for which reaction rate is independent of the concentrations of the reactants; for example, a photochemical reaction in which the rate is determined by the intensity of light.

**Zimm Plot.** A graphical determination of the root-square-mean end-to-end distances of coillike polymer molecules during scattered-light photometric analyses.

**Zone Melting Crystallization.** A method for purification of crystalline solids; the sample, packed in a narrow column, is heated so that a molten zone passes down through the sample, carrying impurities with it.

**Zoning.** A variation in the composition of a crystal from core to margin due to a separation of the crystal phases during its growth by loss of equilibrium in a continuous reaction series.

**Zsigmondy Gold Number.** The number of milligrams of protective colloid necessary to prevent 10 milliliters of gold sol from coagulating when 0.5 milliliter of 10% sodium chloride solution is added.